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THE JOURNAL OF THE FRANKLIN INSTITUTE completes, with the December number, one hundred years of uninterrupted publication. Since the earliest days of the Institute, the JOURNAL has served its designed purposes of reporting to the community the activities of the Institute, and of disseminating knowledge of science and the arts. It has ever been one of the potent agencies of America for making known the advancement of science and the progress of invention.

During those years, science has changed in both character and method of attack. It has ceased to be largely, if not wholly, descriptive and has become, especially in its physical and chemical branches, extremely analytical. Some of its most brilliant successes are won by the methods of mathematical analysis.

The journals purporting to report the course of scientific development have been compelled to alter their forms of expression and to use the changing language of science in the interest of efficiency and of full representation. They have been forced to adopt the notation of mathematics

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by the application, by investigators, of mathematical processes in their thinking and in their experimentation. These changes have placed upon the readers of the journals a burden which has not always been received with calmness, nor borne in silence. But they have been amply justified by the brilliancy of the results obtained by the investigators, and by the completeness of representation by the journals of all scientific thought.

An appreciation of the need for, and value of, research is a marked feature of industrial managements as well as of scientific workers. With this appreciation have come a great increase of research workers and a dire need for the reporting of the results gotten by them. This expansion puts upon all scientific journals a justified demand for space in their columns, in the interest of the maximum of publicity and dissemination of knowledge of science. The JOURNAL OF THE FRANKLIN INSTITUTE will be the agency for publication of the researches carried out at the Bartol Research Foundation. It must, perforce, be more largely devoted to research than ever before, at the same time that it continues to deal with matters of wide interest in science. To fulfill its mission, it should not lose its traditional regard for invention and the generalities of science in its newly-found devotion to specific problems of research.

With this number, the JOURNAL OF THE FRANKLIN INSTITUTE, in a new dress, enters upon the second century of its existence. Its record is a proud one. It has kept touch with all the mutations of science and has fulfilled well the purposes of its founders. It shall be the abiding ambition of its editors to make the second century of the life of the JOURNAL OF THE FRANKLIN INSTITUTE worthy of its past.

THE EDITORS.

ZEEMAN EFFECT AND MULTIPLET STRUCTURE.*

BY

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INTRODUCTION.

BARTOL RESEARCH FOUNDATION
Communication No. 1.

THE experimental study of the optical spectra of the gases of the alkali earths and metals has led to the discovery of certain numerical laws which have been of the utmost importance for the unravelling of the spectra of the heavier metals. It has been found possible to express the frequency of the observed lines with the great degree of accuracy demanded by optical measurements as the difference of two series terms of the following form:

$$W = \frac{N}{(n + a + f(n))^2}$$

where N is Rydberg's constant, n has various integral values, a is a constant for any one series and $f(n)$ is a monatomic decreasing function of n. A theoretical derivation of a formula of this type was first given by Bohr in the case of line spectra of hydrogen, where $a = 0$ and $f(n) = 0$. The series spectra of hydrogen is, however, particularly simple on account of the very simple structure of H, which contains in the normal state only one electron revolving around the heavy nucleus. In general, however, most lines of the spectra of the other elements fall into four distinct classes which are named the principal, diffuse, sharp and fundamental series, respectively, corresponding to their appearance and physical behavior. The particular values which the constant a adopts for the principal, diffuse, sharp and fundamental series are generally denoted by p, d, s, and f.

Using this notation, the wave number ν of the lines of the four series is given by difference of two terms in the following way:

* Doctor Bramley's article is the first communication from the Bartol Research Foundation.

For the principal series

$$\nu = R\left[\frac{1}{(1+s)^2} - \frac{1}{(n+p)^2}\right] \qquad n = 2 \cdots$$

diffuse

$$\nu = R\left[\frac{1}{(2+p)^2} - \frac{1}{(n+d)^2}\right] \qquad n = 3 \cdots$$

sharp

$$\nu = R\left[\frac{1}{(2+p)^2} - \frac{1}{(n+s)^2}\right] \qquad n = 2 \cdots$$

fundamental

$$\nu = R\left[\frac{1}{(3+d)^2} - \frac{1}{(n+f)^2}\right] \qquad n = 4 \cdots$$

where the possible values of n are given on the right.

Actually, the forms of the spectra are not always as simple as they have been described. The lines of the series may occur in pairs, known as doublets, in threes as triplets, and in the general type as multiplets. In the case of doublets, each series is duplicated, since the shorter wave-length components of each doublet, taken together, form a series and the longer components a second series of the same kind. This multiplicity arises from the last term of the principal series; on the other hand, the first term of the sharp series is always multiple. The diffuse series is at the same time multiple with the principal series, although twice or more according to the multiplicity of the series. Moreover, the separation of the components in the d term is much smaller than in the p term, while it is vanishingly small in the f term. The multiplicity of the spectra can thus be regarded as due to the multiplicity in the constants p, d and f, while the constant s is always simple.

Besides the natural multiplicity of the lines of a spectrum into various components, each of which satisfies the fundamental Rydberg equation, the individual lines may be broken up into a number of separate components in the presence of a strong magnetic field. This phenomenon—the Zeeman effect—depends only on the type of series s, p, d, etc., and therefore only on the azimuthal quantum number, and not on the radial quantum number n. All lines which belong to the same series, thus, behave similarly, showing identical resolution on the wave number scale. In this way, even when the lines of the different series are

mixed up, they can be allotted to their series when the Zeeman pattern is known.

The change in the series term of any line can be expressed in the form

$$\triangle W = mwg \qquad m = \text{integer}$$

where g is Landé's fundamental factor. According to the simple theory, first given by Lorentz, the factor g should be unity when

$$w = \frac{e}{4\pi mc} h .$$

Where

h = magnetic field intensity;
e = charge on an electron;
m = mass of an electron,

and

c = velocity of light.

However, the case where g has the value unity, called the "normal" Zeeman effect, is found in spectral lines only exceptionally. Most lines show the complex "anomalous" magnetic separation where the factor g takes on various definite values. The values which this factor assumes have been expressed by Landé in the form

$$g = \frac{3}{2} + \frac{\left(\frac{r}{2}\right)^2 - \left(k - \frac{1}{2}\right)^2}{2j(j+1)} .$$

Where

j = integer;
r = multiplicity of the spectrum, *i.e.*,

the number of lines in the multiplet, *e.g.*, for Na.

$r = 2$ (for Sr $r = 3$, etc.),

and

k = azimuthal quantum number.

Practically, all the known types of Zeeman pattern satisfy within the error of observation this empirical relation.

In this paper, we shall derive a somewhat similar formula for the multiplet separations of a line which shows the intimate connection between these two distinct phenomena.

If we set W, the series term of the longest wave-length

component of the multiplet in the absence of any externally applied magnetic field

$$W = \frac{N}{(n + k + f(n))^2}$$

n = radial quantum number,
k = azimuthal quantum number,

which takes the values 1, 2, 3, 4, for the sharp, principal, diffuse and fundamental series terms, respectively.

Then, we shall show that the series term H of any line of the multiplet in the presence of an external magnetic field h—h may very well be zero—can be expressed in the form

$$H = W\left[1 - \frac{j(j+1)}{r^2 - (2k-1)^2} \cdot \frac{KW^{\frac{1}{2}}}{r^k}\right] + mw\left[\frac{3}{2} + \frac{r^2 - (2k-1)^2}{8j(j+1)}\right]$$

if $r^2 \neq (2k-1)^2$.

Where

j now has the significance of the inner quantum number;
r = multiplicity of the spectrum,

and

K = constant which depends on the atomic number only.

From the selection principle that k changes only by ± 1 and j by 0 or ± 1, we can account for the presence of all the known lines in the optical spectrum and further, the separation of the terms of any one series, which depends only on the total quantum number, should vary as $W^{\frac{3}{2}}$ for any one element.

In case $r^2 = (2k-1)^2$, terms of higher order in the inverse expansion which lead to the above value of H must be considered, and we find, as will be shown, that H may be expressed in the form

$$H = W\left[1 - \frac{j(j+1)}{A} KW^{\frac{1}{2}}\right] + \frac{3}{2} mw$$

where A is a constant of the order of unity but small compared with $r^2 - (2k-1)^2 \neq 0$.

In all lines where the magnetic term separation has the form $3/2\ mw$, the multiplet separation of that term must be large compared with the multiplet separation of the other series terms.

ZEEMAN AND MULTIPLET STRUCTURE.

In the quantum theory as developed by Bohr, Sommerfeld and others, three fundamental assumptions are made:

(1) That an electron can describe periodic paths about a

central charge without radiation of energy, the laws of motion being the familiar electrodynamical equations of a charge under the action of electrical and magnetic forces, neglecting, however, those due to the radiation of energy.

(2) That of all these possible paths which appear as solutions of these equations only certain ones are allowed, *i.e.*, those which satisfy the three conditions

$$\int p_i dq^i = n_i h \qquad \begin{matrix} i = 1, 2 \text{ or } 3 \\ \text{but not summed.} \end{matrix}$$

n = integer and h = Planck's constant, the integral being taken over a complete period. Where q^i is the i^{th} generalized coördinate and p_i, the corresponding momentum, is the derivative of the kinetic energy with respect to

$$\dot{q}^i = \frac{d}{dt} q^i \qquad t = \text{time}$$

i.e.,

$$p^i = \frac{\partial}{\partial \dot{q}^i} \left[m a_i \dot{q}^{i^2} \right]$$

a_i = function of the coördinates only.

(3) That emission of energy in the form of radiation takes place only when the electron passes from one stationary state to another and that as a result of such a passage the difference of energy corresponding to the two states is emitted in the form of monochromatic radiation. Thus if W_1 is the energy in the initial state and W_2 that in the final state, the frequency ν of the emitted radiation is determined by the relation

$$h\nu = W_1 - W_2.$$

In this paper, we shall replace the first two postulates by the following:

(1′) An electron can describe periodic paths about a central charge without radiation of energy, these paths being geodesics in a four-dimensional Weyl space.

The equations of motion [2] of the electron can, therefore, be written in the following form:

$$\frac{d^2x^i}{ds^2} + \Gamma^i_{\alpha\beta} \frac{dx^\alpha}{ds} \frac{dx^\beta}{ds} = 0 \qquad \begin{matrix} i = 1 \cdots 4 \\ \alpha \text{ and } \beta \text{ summed.} \end{matrix}$$

where the Γ's are not only function of position, but also of the path, *i.e.*, the Γ's may be expressed in the following form:

$$\Gamma^{\kappa}_{ij} = \frac{g^{\kappa\alpha}}{2}\left(\frac{\partial g_{i\alpha}}{\partial x^j} + \frac{\partial g_{j\alpha}}{\partial x^i} - \frac{\partial g_{ij}}{\partial x^\alpha}\right) + \frac{1}{4}\left(\delta^{\kappa}_{j}\, g_{i\alpha}\frac{dx^\alpha}{ds} + \delta^{\kappa}_{i}\, g_{j\alpha}\frac{dx^\alpha}{ds} - g_{ij}\frac{dx^\kappa}{ds}\right)$$

summed on α.

Where

$$\delta^{\kappa}_{j} = \begin{matrix} 0 \text{ if } \kappa \neq j \\ 1 \text{ if } \kappa = j \end{matrix}$$

and the $g^{\kappa\alpha}$'s are given by the relation

$$g^{\kappa\alpha}\, g_{j\alpha} = \delta^{\kappa}_{j} \qquad \text{summed on } \alpha;$$

the g_{ij}'s being the components of a symmetric covariant tensor of the second order.

A first integral of these equations [1] is

$$e^{\int g_{\alpha\beta}\frac{dx^\alpha}{ds}\,dx^\beta}\, g_{\alpha\beta}\frac{dx^\alpha}{ds}\frac{dx^\beta}{ds} = \text{const.}$$

where the integral is taken along a particular path.

The solution admits a continuous family [3] of periodic paths in this continuum, provided

$$\int g_{\alpha\beta}\frac{dx^\alpha}{ds}\,dx^\beta = n\,h \qquad \begin{matrix} n = \text{integer} \\ h = \text{const.} \end{matrix}$$

where the integral is taken over a complete cycle.

This condition for the periodicity of the solution of the equations of motion which is a natural consequence of 1′ takes the place of the second postulate in the form of the quantum theory developed by Sommerfeld.

If the variables in the equations of motion are separable, then each of the component parts of the above integral must be equal to an integral multiple of the constant h. This resolution of the periodicity condition into its component parts leads at once to the conception of quantizing the fourth dimensional component (temporal) as well as the spatial components.

In this paper we shall show how the introduction of the fourth quantum condition into the first integral—energy inte-

gral—of an electron in an external magnetic field F leads to a formula of the Landé type for the Zeeman separations and also reveals the intimate connection between the Zeeman separations of the components of a multiplet and the multiplet separations themselves.

We shall first consider according to the classical theory the various parts of the magnetic energy in an atomic system composed of an optical electron revolving about a positive charge e: This positive system can be considered as a heavy nucleus of change ne and a system of $n-1$ electrons external to it.

Due to the presence of the external magnetic field F, the magnetic energy of the optical electron is:

(i) The magnetic energy of the optical electron

$$\frac{e}{m}\frac{hF}{4\pi c}\cos\theta_1$$

e = charge on an electron
m = mass of an electron
c = velocity of light
h = Planck's constant

(ii) The magnetic energy of the atomic core (atomrumpf)

$$\frac{e}{m}\frac{hF}{8\pi c}\cos\theta_2$$

(iii) The mutual magnetic effect between the optical electron and the atomic core

$$\frac{e}{m}\frac{hF'}{8\pi c}\cos\theta$$

where F' is the magnetic force originating from the motion of the optical electron around the internal system, θ_1 and θ_2 are the angles between the direction of the magnetic field F and the axis of the path of the optical electron and the atomic core, respectively, while θ is the angle between the two axes.

The first integral of the equations of motion of an electron, revolving about a positive charge E, is

$$H = 2m\left\{\left(\frac{dr}{ds}\right)^2 + r^2\left(\frac{d\theta}{ds}\right)^2 + r^2\sin^2\theta\left(\frac{d\phi}{ds}\right)^2\right\} + g_{44}\left(\frac{dt}{ds}\right)^2$$

$$g_{44} = 1 - \frac{2eE}{r}$$

By substituting for the g_{ij}'s their values from the above

energy equation into the equations of motion, we find that the force acting on the electron is the familiar Coulomb Law.

This equation can be written in the following form, which is more suitable for our purpose:

$$H\left\{1-\frac{1}{H}\left(\frac{dt}{ds}\right)^2\right\}=2m\left\{\left(\frac{dr}{ds}\right)^2+r^2\left(\frac{d\theta}{ds}\right)^2+r^2\sin^2\theta\left(\frac{d\phi}{ds}\right)^2\right\}-\frac{2eE}{r}\left(\frac{dt}{ds}\right)^2$$

In the presence of an external magnetic field F, the above equation has to be modified by the introduction of the various terms belonging to the magnetic energy—taking the case where the electronic and atomic axes are coincident, *i.e.*, $\cos\theta=0$, we find

$$H\left\{1-\frac{1}{H}\left[\left(\frac{dt}{ds}\right)^2-\frac{1}{2}\frac{eF'}{c}r^2\sin^2\theta\left(\frac{d\phi}{ds}\right)\left(\frac{dt}{ds}\right)\right]\right\}$$
$$=2m\left\{\left(\frac{dr}{ds}\right)^2-\frac{3}{2}\frac{eF}{mc}r^2\sin^2\theta\left(\frac{d\phi}{ds}\right)\left(\frac{dt}{ds}\right)\cos\theta_1+r^2\left(\frac{d\theta}{ds}\right)^2+r^2\sin^2\theta\left(\frac{d\phi}{ds}\right)^2\right\}-\frac{2eE}{r}\left(\frac{dt}{ds}\right)^2$$

The equations of motion corresponding to this first integral are found to be identical in the case where the velocities are small, *i.e.*, $\frac{dt}{ds}=1$ with the classical electrodynamical equations of motion.

Before we attempt to integrate this equation, we must be able to express the path invariant $\cos\theta_1$, in terms of the coördinates and their derivatives.

The simplest path invariant which has zero dimensions is

$$1-\frac{g_{ij}\frac{dx^i}{dt}\frac{dx^j}{dt}}{HT}$$

where T is the period of revolution

$$T=\int ds$$

the integral being taken over a complete path.
Since

$$H=g_{ij}\frac{dx^i}{ds}\frac{dx^j}{ds}$$

our energy equation becomes

$$H\left\{1-\frac{1}{H}\left[\left(\frac{dt}{ds}\right)^2-\frac{1}{2}\frac{eF'}{c}r^2\sin^2\theta\left(\frac{d\phi}{ds}\right)\left(\frac{dt}{ds}\right)\right]\right\}$$

$$= 2m\left\{\left(\frac{dr}{ds}\right)^2 + r^2\left(\frac{d\theta}{ds}\right)^2 + r^2\sin^2\theta\left(\frac{d\phi}{ds}\right)^2\right.$$

$$\left. - \frac{3}{2}\frac{eF}{mc}r^2\sin^2\theta\left(\frac{d\phi}{ds}\right)\left(\frac{dt}{ds}\right)\left(1 - \frac{\left(\frac{ds}{dt}\right)^2}{T}\right)\right\} - \frac{2eE}{r}\left(\frac{dt}{ds}\right)^2$$

As ϕ and t are cyclic coördinates of the above equation

$$r^2\sin^2\theta\left(\frac{d\phi}{ds}\right) = \text{const.} = \alpha_3$$

and

$$g_{44}\left(\frac{dt}{ds}\right) = \text{const.} = \alpha_4 .$$

Using these two relations and regarding $\frac{ds}{dt}$ as a constant whose value we shall determine from the fourth quantum condition, we obtain for the energy H after integration

$$H = W\left[1 - \frac{1}{H}\left(\frac{dt}{ds}\right)^2 + \text{term in } F'\right]$$

$$+ \frac{3}{2}n_3\frac{\hbar\omega}{2\pi}\left[1 - \frac{\left(\frac{ds}{dt}\right)^2}{T}\right]$$

$$\omega = \frac{eF}{2mc}$$

W = the energy of the electron according to the Bohr-Sommerfeld theory.[4]

In deriving this form for the energy H of the optical electron, we have used the three spatial quantum conditions

$$\int p_r dr = n_1 h$$

$$\int p_\theta d\theta = n_2 h$$

$$\int p_\phi d\phi = n_3 h$$

We shall now make use of the fourth condition

$$\int g_{44}\left(\frac{dt}{ds}\right)^2 ds = n_4 h$$

to determine the value of $\frac{dt}{ds}$ appearing in the equation for the energy H of the optical electron.

Since

$$g_{44}\left(\frac{dt}{ds}\right) = \text{const.}$$

the integral

$$\int g_{44}\left(\frac{dt}{ds}\right)^2 ds$$

can be expressed in the form

$$g_{44}^2\left(\frac{dt}{ds}\right)^2 = \frac{n_4 h}{\int \frac{ds}{g_{44}}}$$

or

$$\left(\frac{dt}{ds}\right)^2 = \frac{n_4 h}{Tf},$$

where f is a function which we shall subsequently consider in more detail.

Thus our equation for H becomes

$$H = W\left[1 - \frac{n_4\kappa}{f} W^{\frac{1}{2}} + \text{term in } F'\right] + n_3 \frac{h\omega}{2\pi}\left[\frac{3}{2} - \frac{3f}{2n_4 h}\right]$$

where

$$\kappa W^{\frac{1}{2}} = (TH)^{-1}.$$

This constant κ, which enters into the above equation, depends on the atomic number and the type of multiplicity of the spectrum.

The integer n_4, which appears here, is connected with the inner quantum number j by the relation

$$n_4 = \frac{j}{2}(j+i).$$

Substituting for n_4 in terms of j, we have

$$H = W\left[1 - \frac{j(j+1)}{2f}\kappa W^{\frac{1}{2}} + \text{term in } F'\right] + n_3 \frac{\omega h}{2\pi}\left[\frac{3}{2} - \frac{3f}{j(j+1)}\right].$$

Using the Bohr frequency condition—postulate iii—we have in the case $F = F' = 0$ for the frequency of two lines arising from the same initial state H_1 but two different end states H_2 and H_2' where the end states have the same value of W but different j's,

$$h\nu = H_1 - H_2$$

and

$$h\nu' = H_1 - H_2'$$

so that the frequency separation of the two lines of the multiplet is

$$h(\nu - \nu') = H_2 - H_2'$$
$$= W\left(1 - \frac{j(j+1)}{2f}\kappa W^{\frac{1}{2}}\right) - W\left(1 - \frac{j'(j'+1)}{2f}\kappa W^{\frac{1}{2}}\right)$$
$$= -\frac{\kappa W^{\frac{1}{2}}}{2f}\left[j(j+1) - j'(j'+1)\right].$$

Using the values of j, associated with the various levels, the triplet separation ought to be

in the p series as 1 : 2
in the d series as 2 : 3.

In the case $f \doteq 0$ we have to use the complete expression for the fourth quantum condition

$$\int \frac{eF}{c}\left[\frac{3}{2} + \frac{F'}{F}\cos^{-1}\theta_1\right] r^2 \sin^2\theta \cos\theta_1 \frac{d\phi}{ds}\frac{dt}{ds}\,ds$$
$$+ \int g_{44}\left(\frac{dt}{ds}\right)^2 ds = n_4 h$$

If $F' >> F$ then in this case where $f \doteq 0$

and $\therefore \quad \int g_{44}\left(\frac{dt}{ds}\right)^2 ds \doteq 0$

$$\frac{e}{c}F' \int r^2 \sin^2\theta \frac{d\phi}{ds}\frac{dt}{ds}\,ds = n_4 h$$

or $$\frac{e}{c}F'\alpha_3 \int \frac{dt}{ds}\,ds = n_4 h$$

or $$\frac{e}{c}F'\left(\frac{dt}{ds}\right) = \frac{n_4 h}{\alpha_3 T} = \frac{2\pi n_4}{n_3 T}$$

since $$\int p_\phi d\phi = 2\pi\alpha_3 = n_3 h.$$

Substituting this value in the equation for H, we find

$$H = W\left[1 - \frac{n_4}{A}\kappa W^{\frac{1}{2}}\right] + \frac{3n_3\omega h}{4\pi}$$

the term in $\left(\frac{dt}{ds}\right)^2$ being neglected in comparison with

$$\frac{e}{c}F'\alpha_3\left(\frac{dt}{ds}\right)$$

for the relation

$$g_{44}^2\left(\frac{dt}{ds}\right)^2 \int \frac{ds}{g_{44}} \doteq 0$$

requires that $\left(\frac{dt}{ds}\right)^2$ is approaching zero.

The constant A must be much smaller than f in all cases where f is not zero. In the actual spectral series this condition is fulfilled in all cases where the data were available.

We shall now consider more fully the significance of the function f which appears in our equations

$$f = \frac{g_{44}^2}{T} \int \frac{ds}{g_{44}}$$

The energy equation, $Hds^2 = g_{ij}dx^i dx^i$, together with the condition,

$$\int Hds = \sum_{i=1}^{4} pn_i$$

do not determine H uniquely, for we can subject s to an arbitrary change of guage

$$ds \rightarrow \lambda ds$$

and derive a new energy function $H = \lambda^2 H$, which satisfies these conditions.

The function f, however, may be used to define a unique energy and can therefore be considered as a further restriction on our problem besides the four-quantum conditions.

Referring to Landé's empirical rule for the Zeeman effect, we find

$$\frac{3}{2}f = \frac{3}{2} g_{44}^2 \frac{\int \frac{ds}{g_{44}}}{T} = r^2 - (2k-1)^2$$

so that our equation for the energy of the stationary states becomes

$$H = W\left[1 - \frac{j(j+1)}{r^2-(2k-1)^2}\kappa W^{\frac{1}{2}}\right] + \frac{n_3 \omega h}{2\pi}\left[\frac{3}{2} - \frac{r^2-(2k-1)^2}{8j(j+1)}\right]$$

where κ is a constant for any particular element and type of path, *i.e.*, it depends on the atomic number N and on the quantum integers k and r.

Using the above formula for the energy levels in the atom, we find for the ratio of the p and d separations of Cr, regarding κ as a constant and using the first term of the series

$$\frac{\delta W_d}{\delta W_p} = \frac{\frac{2}{21}}{\frac{1}{5}}\left(\frac{W_d}{W_p}\right)^{\frac{1}{2}} = .36 +$$

$$= \frac{97.9}{554} = .18 \text{ experimentally.}$$

For the Ca^+ doublets

$$\frac{\delta W_d}{\delta W_p} = \frac{10}{21}\left(\frac{W_d}{W_p}\right)^{\frac{1}{2}} = .60$$

$$= \frac{61}{223} = .28 \text{ exp.}$$

For the Sr triplets, d and f series,

$$\frac{\delta W_f}{\delta W_d} = \frac{48}{80}\left(\frac{W_f}{W_d}\right)^{\frac{1}{2}} = .081$$

$$= \frac{2.7}{100.5} = .027 \text{ exp.}$$

For the Sr p triplets, we have an example of the case

$$r^2 - (2k-1)^2 = 0$$

For Sr^+ doublets

$$\frac{\delta W_d}{\delta W_p} = \frac{10}{21}\left(\frac{W_d}{W_p}\right)^{\frac{1}{2}} = .60$$

$$= \frac{279}{801} = .35 \text{ exp.}$$

For the Ba^+ doublets

$$\frac{\delta W_d}{\delta W_p} = \frac{10}{21}\left(\frac{W_d}{W_p}\right)^{\frac{1}{2}} = .60$$

$$= \frac{576}{1689} = .33 \text{ exp.}$$

Since Ba is non-Ritzean, we cannot employ the above equation to calculate the values of the separations.

The above data show that the energy of the various levels in the atom can be written in the form

$$H = W\left[1 - \frac{j(j+1)}{r^2-(2k-1)^2}\frac{K}{R^k}W^{\frac{1}{2}}\right] + \frac{n_3\omega h}{2\pi}\left[\frac{3}{2} - \frac{r^2-(2k-1)^2}{8j(j+1)}\right]$$

where K now is a constant which depends on the atomic number only, and where $R = r$ for the alkali earths and metals.

In conclusion, I wish to acknowledge my indebtedness to Prof. E. P. Adams, of Princeton, and W. F. G. Swann, of Yale, for their many suggestions and general encouragement.

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[2] EISENHART: *Nat. Acad. of Sc.*, June, 1923.
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BARTOL LABORATORIES OF
THE FRANKLIN INSTITUTE.

Use of Sodium Nitrite in Curing Meats.—W. LEE LEWIS, R. S. VOSE, and C. D. LOWRY, JR., of the Institute of American Meat Packers (*Ind. and Eng. Chem.*, 1925, **17**, 1243–1245), have studied, on a commercial scale, the use of sodium nitrite in the curing of hams, bacon, tongues, and beef. Their results indicate that the sodium nitrate (saltpetre), which is usually used as a constituent of the pickling solution, may be replaced successfully by one-tenth its weight of sodium nitrite. J. S. H.

Salt Craving.—NORMAN J. HARRAR, of the Colorado Agricultural College (*Jour. Chem. Education*, 1925, **2**, 1054–1058), discusses the theory of salt craving, or the requirement of animals for sodium chloride. The theory that this requirement of the animal increases with the potassium content of the food is shown to be contrary to the facts. The salt requirement depends on the chloride ion content of the food, the potential acidity or basicity of the diet, and its water content. If the food be potentially basic, a craving is created for a substance which supplies strong acid ions; and this craving is satisfied by sodium chloride. If the food be rich in water, it is poor in chlorides, and a craving for sodium chloride results, just as ingestion of a large amount of salt gives rise to a thirst for water. J. S. H.

Instruction in Chemistry in America.—HARVEY W. WILEY (*Jour. Asso. Official Agric. Chem.*, 1925, **8**, 646–653), in the course of an address before that Association, states that the history of instruction in chemistry in the United States may be divided into three epochs. During the first epoch, all instruction was given by means of a text-book; at times, this instruction was supplemented by demonstrations and lectures. During the second epoch, the student received practical instruction in the laboratory as well as studied a text-book. This laboratory instruction was given at Princeton University for a year or two before 1800, at the College of William and Mary in 1807, and at Harvard University in 1854 or 1855. Wiley introduced laboratory instruction into Indiana, into Butler College in 1873 and into Purdue University in 1874. The third epoch includes work in synthesis and research. It began in this country during the last quarter of the nineteenth century. J. S. H.

STANDARD ELECTRICAL CELLS.*

BY

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THE volt is defined, of course, in both the electrostatic and electromagnetic systems of fundamental units. However, since the electrostatic system is founded upon the force between two statical electric charges, the units of this system are not the ones most suitable for dealing with dynamical applications of electricity. On the other hand, the means of realizing the volt as defined by the electromagnetic system are too intricate and ponderous to be adapted to use anywhere but in a laboratory devoted to highly specialized investigations of fundamental electrical units.

Of all the combinations which give rise to an electromotive force, a voltaic cell seems to be best suited for the basis of electromotive force comparisons. Therefore, since the volts of the absolute systems are not suitable in practice, some type of cell, calibrated with greater or less accuracy in terms of the ohm and the ampere, has long served as a practical standard.

The principal ones of these cells, either of actual or of historical interest, are given in Table I.[1]

Before proceeding to a consideration of the suitability of the elements listed, it will be well to run over the conditions that several investigators hold should be fulfilled by a satisfactory standard.

Jaeger, in the first chapter of his classical work "Die Normalelemente und ihre Anwendung in der elektrischen Messtechnik," says: "The following conditions must be laid down for normal elements, regarding as such in the narrower sense only hydroelements with metal electrodes:

"(1) Their electromotive forces must remain constant under the same external conditions (of temperature) and

"(2) Their electromotive forces must not be changed either by the withdrawal of current from the system, or the passage

* Presented at a meeting held Thursday, November 5, 1925.

[1] GLAZEBROOK, "Dict. Applied Physics," Vol. 2, p. 260.

of current through it, when the current does not exceed a certain fixed value for each type of cell, as well as that

"(3) They must be reproducible."

He gives also the following definition: "A normal element is a reversible chemical system in equilibrium having constant phases: In our special case it is a system with an aqueous solution as the electrolyte, and with metal electrodes."

Reinders,[2] however, points out that two metal phases can be

TABLE I.

Name.	Positive Element.	Depolarizer.	Electrolyte.	Negative Element.
Daniell	Copper	Copper sulphate	Sols. zinc sulphate and copper sulphate	Zinc
Fleming type of Daniell	Copper	Copper sulphate	Sols. zinc sulphate and copper sulphate	Zinc
Clark	Mercury	Mercurous sulphate	Sat. sol. zinc sulphate	Zinc amalgam
Clark-Carhart	Mercury	Mercurous sulphate	Sol. zinc sulphate	Zinc amalgam
Gouy	Mercury	Mercurous oxide	Sol. zinc sulphate	Zinc
De la Rue	Silver	Silver chloride	Sol. zinc chloride	Zinc
Helmholtz	Mercury	Mercurous chloride	Sol. zinc chloride	Zinc
Hibbert	Mercury	Mercurous chloride	Sol. zinc chloride	Zinc
Weston	Mercury	Mercurous sulphate	Sol. cadmium sulphate	Cadmium amalgam
Normal Weston	Mercury	Mercurous sulphate	Sat. sol. cadmium sulphate	Cadmium amalgam

in equilibrium with the same electrolyte only when they are in equilibrium with each other; and in such a case the electromotive force would be zero. In the light of this statement Jaeger's definition obviously is not accurate in its entirety.

According to van Ginneken and Kruyt,[3] in terms of the phase rule, a normal element consists of two four-phase systems of the same four components. They say further that in order that the e.m.f. may not be affected it is necessary that the diffusion velocity shall be lower than the velocity with which the equilibrium in either side of the system establishes itself. For current, this of

[2] REINDERS, *Zeit. phys. Chem.*, **42**, 232.

[3] VAN GINNEKEN and KRUYT, *Zeit. phys. Chem.*, **77**, 744 (1911).

course need hold only for definite but practical limits of current intensity. In addition, if the passage of a current in either direction, or diffusion, sets up on both sides of the combination an invariant (p.t.) system of the components present, the e.m.f. will remain constant. In connection with the diffusion it is necessary that on both sides the same components be found.

Two researches, that of Ogg and that of Hulett and DeLury, throw much light on what the equilibrium conditions in a standard cell are.

Ogg [4] determined the actual quantities of silver deposited in mercury when this element had come to equilibrium with a solution of a silver salt. From his data, he concluded that the equilibrium between metals and their aqueous solutions can be calculated by the Nernst formula:

$$\sqrt[n_1]{\frac{P_1}{p_1}} = \sqrt[n_2]{\frac{P_2}{p_2}}.$$

The fact that this formula is valid infers the validity of the reasoning by means of which it is derived. The gist of this reasoning, as outlined by Ogg, is as follows: For a mixture of two metals (an amalgam, an isomorphous mixture, or a mechanical mixture) to be in equilibrium with an aqueous solution, we must think of one metal going into solution, while at the same time an equivalent quantity of the other separates out.

Hulett and DeLury [5] discovered as the result of an investigation of the reduction of cadmium by mercury, that below a cadmium concentration of $1/10^6$ there is a deviation that conforms to the hypothesis that at equilibrium there remains some mercury in the solution.

With the work just noted in mind, let us now consider what should happen in a cell made up as follows: A cadmium amalgam—a solution of a salt of cadmium—an excess of the salt of mercury corresponding to the salt of cadmium—mercury.

When the combination is first set up, mercury from the amalgam must go into solution until equilibrium is established. On the mercury side the solid mercury salt goes into solution until this solid phase and its solution are in equilibrium. Now, if the equilibrium concentration of mercury at the amalgam surface

[4] OGG, *Zeit. phys. Chem.*, **27**, 285 (1893).
[5] HULETT and DELURY, *J. Am. Chem. Soc.*, **30**, 1805.

be lower than the concentration due to the solubility of the mercury salt, mercury from this latter diffuses over to the amalgam pole, where the mercury concentration being made greater than the equilibrium value by this new arrival, mercury must separate out, and cadmium go into solution. If, on the other hand, the equilibrium concentration of mercury at the amalgam pole be greater than that due to the excess of mercury salt, mercury from the amalgam pole will diffuse over to the excess of mercury salt, increasing there the concentration of the mercury ion in contact with the solid salt. As this higher concentration cannot persist in the presence of the solid salt, mercury salt must solidify out upon this excess. As this must upset the equilibrium, more mercury from the amalgam must go into solution and cadmium from the solution separate out. These transformations will continue until a uniform concentration throughout is established, even though the cell be upon open circuit. Quite naturally, the changes can be made to take place with exceeding slowness.

It need scarcely be suggested that the appropriate ions in the solution play the leading rôles in the carrying through of the above cycles, and the outline sketched therefore can be taken only as a broad statement of the net results. But if this reasoning is correct, it is submitted that a cell like that described cannot be in equilibrium unless the concentration of the mercury, due to the excess of salt, equals the equilibrium concentration of mercury due to the amalgam.

It has been shown, as will be stated later, that the e.m.f. of the Weston or unsaturated cadmium cell drifts downward slightly with time and is not, therefore, in equilibrium. The cause of this fall in e.m.f. is, almost without question, an increase in the concentration of the electrolyte due to the gain in the solution of cadmium ion brought about by the displacement from solution of mercury by cadmium of the amalgam. I know of no experimental data proving this point however.

When an excess of the salt of the metal of the amalgam is in contact with the solution, no change in e.m.f. due to a change of concentration can occur. The normal cadmium cell has such an excess of solid salt, and to this the greater constancy of the normal cell is ascribed. The e.m.f. will remain constant, as long as the solid salt of mercury (mercurous sulphate, the depolarizer) is not

exhausted on the one hand, and the cadmium concentration of the amalgam is not too far reduced upon the other. Such behavior is in conformity with the definitions of van Ginneken and Kruyt, above.

Returning to our list of standards, we find first upon it the Daniell, and the Fleming type of Daniell, cells. Both of these consist of a zinc electrode in a solution of zinc sulphate, in contact with a copper sulphate solution in which is a copper electrode. The container of the Fleming cell is a glass U-tube with a stop-cock for drawing off the copper sulphate solution when the cell is not in use. Both salts are very soluble, hence diffusion is rapid, and the copper sulphate attacks the zinc electrode rapidly.

The Gouy cell is not reversible. When current is passed through it, mercurous sulphate is formed.

The De la Rue, Helmholtz, and Hibbert cells all have a mutual disadvantage. All three contain zinc chloride (zinc butter), a very poorly defined substance chemically. With regard to the Helmholtz cell it is interesting to note that Ostwald,[6] and also Schoop, tried to produce a standard having an e.m.f. of one volt by regulating the concentration of the zinc chloride solution. Ostwald recommended one having a density of 1.409 at 15°: Schoop, one having a density of 1.391 at the same temperature.

We have left only the two Clark cells, and the two Weston elements.

Before going further, specific mention should be made of the two types of cell in use, the "normal" and the "unsaturated." The normal cell has an excess of the salt of the metal of the amalgam; the solution of the "unsaturated" cell is in equilibrium with the solid phase of this salt at a temperature considerably lower than those usually met in the laboratory.

The Clark cell consists of zinc amalgam (7–10 per cent.), saturated solution of zinc sulphate with excess of crystals, mercurous sulphate, and mercury; the Clark-Carhart, of the same system without excess of zinc sulphate. The first is reproducible, and both are constant. The Clark, however, has a high temperature-coefficient, about 0.00119 volt per degree centigrade. This would not be a deciding disadvantage in view of its constancy and reproducibility, as the temperature could be controlled and temperature effects eliminated. The Clark-Carhart element has a

[6] JAEGER, "Die Normalelemente," p. 74.

lower temperature-coefficient, about .00053 volt per degree centigrade. The e.m.f. of the Clark is 1.4326 international volts at 15° C. and that of the Carhart about 1.4328 volts at 15°. The zinc salt in the two cells is $ZnSO_4.7H_2O$, which is transformed into $ZnSO_4.6H_2O$ at the inconveniently low temperature of 39° C. The disadvantages of these zinc-amalgam cells are the tendency of the glass containing-vessel to break, due to the expansion of the sealed-in platinum lead-wires through alloying with the zinc, the formation of bubbles of hydrogen which open the internal circuit, and the caking of the solid $ZnSO_4$.

McKelvy and Shoemaker [7] state that 120 out of 128 Clark cells set up in 1906 were useless in 1921 because of cracking at the amalgam limb, or open circuiting because of gas. Hulett [8] experienced the same difficulties. By subjecting the wires to the action of a zinc amalgam before sealing into the glass, the first two authors seem to have eliminated cracking. The deleterious effects of gas formation they reduced to a minimum by using only a small excess of the solid salt, thus preventing the "trapping" of the gas-bubble. These inconveniences, absent in the cadmium or Weston cell, have been sufficient to bring about the general adoption of this latter, which has the desired constancy when properly made, and in addition a lower temperature-coefficient.

In 1892, Dr. Edward Weston proposed his cadmium cell. This consists of a cadmium amalgam, a solution of cadmium sulphate saturated at about 4° C. and an opposite pole of mercury covered with solid mercurous sulphate.

It soon appeared that there were a number of factors which produced irregularities in the e.m.f. of this combination as will be seen from the following extract from a letter written by the Bureau of Standards under date of February 29, 1916.

"We have tried the effect of various added impurities on cells but without any very definite results, owing to the fact that cells set up with materials from the same lots at different times have not *always* given the same electromotive forces, nor shown the same behavior.

"As soon as we are sure that we can reproduce cells which have the same electromotive force and which will hold their

[7] McKELVY and SHOEMAKER, Bur. Stan. Sci. Papers 390, p. 411, 1921.
[8] HULETT, *Phys. Rev.*, **32**, 3, 272 (1911).

values for a long time, which, as stated above, is at present not always the case, we will be in a position to obtain specific data regarding the effects of added impurities."

It is to the major of these irregularities, their causes, and the attempts to eliminate them that the remainder of this paper will be devoted, with such incidental descriptions of methods and the like as may be required. I will endeavor to gather the conclusions of various investigators into appropriate groups.

Various forms of container for standard cells have been proposed,[9] but the vessel in practically general use is that recommended by Rayleigh. This is an H of glass tubing; the lower ends of the upright tubes being sealed off, and almost invariably provided with fused-in platinum wires, to make electrical contact with the contents. The solid contents may be held in place by septa of cork, covered with linen,[10] or by some more elaborate device, say a porcelain plug, wrapped with cotton or asbestos. Such plugs are usually held in position by two corks sealing the mouths of the H-tubes. Cork discs or septa, covered with linen, are simple, seem to be satisfactory, and permit the mouths of the H-tube to be sealed in the blow-flame after filling. This insures absolutely against concentration of the electrolyte by evaporation, which sometimes occurs when a cork and some sort of cement are used to make the cell tight. Cells without septa are almost invariably made for primary standards. Roughly, this description pictures the "portable" and the "non-portable" types of cell.

The mercury used in standard cells should be purified by letting it run in a very fine spray through a column of dilute nitric acid.[11] After this, it should be distilled under reduced pressure, in a stream of air.[12] The presence of air, even in a small amount, oxidizes any zinc, cadmium, bismuth, tin, copper, lead, etc., that may be present. The gold, silver and platinum remain in the flask. Two distillations by this method reduced a saturated solution of silver in mercury to a silver concentration of less than two parts in a million.

[9] WRIGHT, *Phil. Mag.*, 16 (1883). DELURY, *Phys. Rev.*, 25, 492 (1907). COHEN and KRUYT, *Zeit. phys. Chem.*, 72, 38 (1910). HULETT, *Phys. Rev.*, 32, 273 (1911). RODMAN and SPOONER, *Trans. Am. Electrochem. Soc.*, 38 (1920). ISHIBASHI, "Researches Electrotech. Lab." (Japan), 113 (1922).

[10] WESTON, *Elect.*, 30, 741 (1893). TINSLEY, *Elect.*, 65, 568 (1910).

[11] L. MEYER, *Zeit. Anal. Chem.*, 2, 241.

[12] HULETT, *Phys. Rev.*, 33, 4, 314 (1911).

The cadmium amalgam is made by dissolving the required weight of pure cadmium in an appropriate weight of pure mercury on a steam bath. It can also be prepared by placing a weight of mercury in a dish, placing over it the weight of cadmium sulphate crystals that contain the required amount of cadmium, covering the whole with a moderately dilute solution of sulphuric acid and electrolyzing until the cadmium is all deposited in the mercury.[13] The usual percentage of cadmium in the amalgam is 12.5, although a 10 per cent. amalgam is often used.

Cadmium sulphate crystallizes with 8/3 molecules of water. It is stable up to 74° C. Apparently, it is not isomorphous with any substance, so can be procured in a high state of purity by one or two recrystallizations. The most satisfactory salt I have been able to secure as a basis for the cells made in my laboratory is one supplied to the ceramics industry. It contains manganese in very small quantities, but even one recrystallization seems to remove this. Wolff and Waters[14] give the possible impurities in commercial chemically pure cadmium sulphate as zinc, lead, ferrous and ferric iron, and occasionally nickel. They do not mention manganese. Manganese seems to raise the value of the electromotive force and to lower the internal resistance of cells. Cells containing it have not been as constant as those made with a purified salt. The experiments upon which these statements are based were not extensive, so must be taken as qualitative only.

The electrolyte is a saturated solution of cadmium sulphate for normal cells, or a solution saturated at about 4° for the unsaturated type. Cadmium sulphate is a very soluble salt, but the rate at which it goes into solution is slow. The solubility varies but slightly with temperature.[15] Our practice is to stir by a motor-driven glass paddle-wheel, in a thermostat maintained at 25° ± 05, a solution of cadmium sulphate in contact with an excess of solid salt. When this has run long enough to have insured saturation, we remove some of the solution and determine its density with a Westphal balance. If, due to some disturbance, the density is lower than that corresponding to saturation,

[13] HULETT, *Phys. Rev.*, **32**, 3, 270 (1911).
[14] WOLFF and WATERS, Bur. Stan. Bull., **4**, 14 (1907–1908).
[15] HULETT, *Phys. Rev.*, **32**, 3, 268 (1911).

we continue stirring until a density determination shows saturation to have been reached.

At this point, anyone interested in standard cells will find that he has to choose between two schools of thought—that of the adherents of a neutral solution, and that of those who believe an acid solution to be necessary for the production of a constant cell. Our experience has been that only cells with acid concentrations lying between certain limits can be relied upon to be constant. We therefore prepare an aqueous solution at least 0.015 molar with sulphuric acid, for normal cells and saturate this with cadmium sulphate. By the addition of a more concentrated aqueous solution of sulphuric acid to the saturated neutral solution of cadmium sulphate first mentioned, we bring this up to about 0.04 molar for use in unsaturated cells. At the same time this addition reduces the saturation of the solution to about that corresponding to 4° C.

Mercurous sulphate can be either white or gray, due to finely divided reduced mercury. It can be prepared in a number of ways, as given by Wolff and Waters:[16]

(1) By electrolysis.
(2) By the action of fuming sulphuric acid on mercury.
(3) By the reaction between sulphuric acid and mercurous nitrate.
(4) By the action of a dilute solution of nitric acid in sulphuric acid on mercury.
(5) By the reduction of mercuric sulphate by mercury.
(6) By the reduction of mercuric sulphate by sulphurous acid.
(7) By the recrystallization of commercial mercurous sulphate from sulphuric acid.

Another method is the reduction of mercuric sulphate, made from mercuric oxide, by formaldehyde.[17] This I have tried out quite thoroughly, and it can be made to give excellent results. I have used all of these methods except number seven myself, and Doctor Vosburgh, who has devoted most of three years in my laboratory to research upon standard cells, also has tried out most of them. It has been my experience that reduction methods in general produce cells that usually agree well within a group, and are constant; but that such cells show unexpected and sudden changes in voltage. For instance, a group of ten cells will show a very close agreement with the standard value, say to ten microvolts for weeks, after they are newly made. Then without warn-

[16] WOLFF and WATERS, Bur. Stan. Bull., **4**, 15 (1907–1908).
[17] VOSBURGH and EPPLEY, *J. Am. Chem. Soc.*, **45**, 10, 2269 (1923).

ing, one cell will drop thirty or forty microvolts. After a time, sometimes only a day, such a cell will usually come back to normal. Mercuric sulphate reduced by formaldehyde at the boiling temperature is an exception to this statement.

A very simple way to prepare white mercurous sulphate is to allow a solution of mercurous nitrate in dilute nitric acid to drop slowly into a well-stirred solution of sulphuric acid.[18] I have made many cells with freshly prepared salt so made, and have found them to be very constant. In fact, after a period of ageing, they were as good as cells could be expected to be. However, if this same salt, even though thoroughly washed, were allowed to stand under a 1 to 6 sulphuric acid solution, there would be a copious evolution of brown fumes in a few days. Cells made with the salt after this evolution would have abnormal, usually very low values, and would not become constant.

I have always ascribed abnormal behavior of these two types to the existence of inclusions in the grains of mercurous sulphate, although I know of no research upon cells to confirm this opinion. Cox[19] mentions the effect of inclusions in his paper upon the equilibria among mercury salts.

Mercurous sulphate can be prepared best by the electrolysis of a sulphuric acid solution with an anode of mercury,[20] a process developed independently of each other by Hulett and by Wolff.[21] It is essential that the solution be well stirred over the surface of the mercury, since if it is not basic mercurous sulphate is apt to form. In the Hulett apparatus, the surface of the mercury was but gently agitated.[22] Wolff and Waters[23] modified the apparatus and stirred so that "the mercury is vigorously rotated without being broken up into small globules." By using direct or alternating current (this latter with a further modification of the apparatus), by varying the rate of stirring, and by using different current densities, products running from white to dark gray can be secured. The dark gray compound, owing its color to globules of finely divided mercury, undoubtedly gives the best results in standard cells. Any mercurous sulphate so made should

[18] WOLFF and WATERS, Bur. Stan. Bull., **4**, 21 (1907–1908).
[19] Cox, *Zeit. anorg. Chem.*, **40**, 180 (1904).
[20] CARHART and HULETT, *Trans. Am. Electrochem. Soc.*, **5**, 59.
[21] WOLFF, *Trans. Am. Electrochem. Soc.*, **5**, 56.
[22] HULETT, *Phys. Rev.*, **32**, 3, 262 (1911).
[23] WOLFF and WATERS, Bur. Stan. Bull., **4**, 19 (1907–1908).

be digested upon the steam bath under 1 to 6 sulphuric acid for at least four days, in order to insure uniformity of grain-size.

Mercurous sulphate undergoes hydrolysis very readily. It should therefore be kept under 1 to 6 sulphuric acid in the dark, as it is also light-sensitive, turning gray, seemingly with formation of mercuric salt.[24]

The effect of the grain-size of the mercurous sulphate upon e.m.f. has been mentioned by Steinwehr,[25] who attributed the irregularities laid by Hulett to hydrolysis to differences in the size of the depolarizer particles.

F. E. Smith[26] found, for grain-sizes between 3 and 30 microns, that the variation in e.m.f. was slight, 1.01828–1.01831 volts. He concluded that crystals between 3–30 microns have the same solubility and give the same e.m.f. The size of his particles was usually between 5 and 30 microns.

Wolff and Waters[27] say that "the close agreement of the numerous samples prepared by different methods and under varying conditions shows that any effect due to size of grain may be disregarded."

Vosburgh and Eppley[28] investigated mercurous sulphate containing grains as large as 360μ by 170μ in certain samples and as small as 3μ with no large grains in others. They found that cells with finely divided depolarizer had e.m.f.s 40 to 100 mv. higher than cells made with coarser mercurous sulphate. They hold that a large grain is better for primary standards as it more nearly reproduces the accepted value. By "large grain" is meant a preparation having a number of grains as long as 110μ to 240μ mixed with smaller grains say 5μ long. Such dimensions must of necessity be the merest approximations.

An opposite view is expressed by Hulett,[29] who says that "not only is the effect of the size of the particles not to be feared in constructing the cadmium cell, but it may be concluded that a rather fine-grained paste of good depth would give the most constant results . . ."

It has been noted already that there is a difference of opinion

[24] GMELIN-KRAUT, *Handb. d. anorg. Chem.*, **5**, 2, 597.
[25] STEINWEHR, *Z. Electrochem.*, **12**, 578 (1906).
[26] SMITH, *Trans. Roy. Soc.* (London), A, 207, 401 (1908).
[27] WOLFF and WATERS, Bur. Stan. Bull., **4**, 72 (1907–1908).
[28] VOSBURGH and EPPLEY, *J. Am. Chem. Soc.*, **46**, 1, 111 (1924).
[29] HULETT, *Trans. Am. Electrochem. Soc.*, **64**, 65 (1908).

in the literature as to the effect of acid in the electrolyte of a cadmium cell. Wolff and Waters[30] say " . . . that the greatest care must be taken in washing the sample (of mercurous sulphate) to completely remove all traces of acid." Hulett[31] says " the problem (in making the paste) is to prepare a mixture of mercurous sulphate, . . . cadmium sulphate and saturated solution, but to avoid the presence of sulphuric acid . . ." Shaw and Reilley[32] warn against acidity in the mercurous sulphate. " Green feathery streaks " in the paste they attribute to acidity.

On the other hand, Hulett[33] found that Weston cells with acid electrolytes were remarkably constant in electromotive force, and F. E. Smith[34] and Obata[35] have observed that Weston normal cells were more constant if the electrolyte were acid than if it were neutral. (Mr. F. E. Smith told me in conversation that the custom at the National Physical Laboratory had been to saturate a 0.1 normal solution of sulphuric acid with cadmium sulphate for use in normal cells.) Vosburgh and Eppley[36] made neutral unsaturated cells which were less regular in behavior than acid cells made of the same materials except for the addition of acid.

Hulett, in 1906,[37] stated that mercurous sulphate in cadmium sulphate solution was not in equilibrium. He tested the matter out as follows: He first made a dissectable cadmium cell, the amalgam pole of which he could remove and connect with a tube containing cadmium sulphate solution, mercurous sulphate, and mercury. As this mercury was in contact with a sealed-in platinum wire, such a tube constituted a mercury leg identical in all practical respects with that of a cadmium cell. He was thus in possession of a means of comparing such a number of these mercury limbs as he chose with the same cadmium amalgam leg, which last could be maintained under conditions designed to insure its constancy. With its own mercury pole, this reference amal-

[30] WOLFF and WATERS, Bur. Stan. Bull., **4**, 28 (1907–1908).
[31] HULETT, *Phys. Rev.*, **32**, 3, 265 (1911).
[32] SHAW and REILLEY, *Trans. Roy. Soc. Canada*, **13**, Sect. iii, 174 (1919).
[33] HULETT, *Trans. Am. Electrochem. Soc.*, **14**, 89 (1908).
[34] F. E. SMITH, *Elect.*, **75**, 463 (1915).
[35] OBATA, *Proc. Math. Phys. Soc., Japan*, **2**, 232 (1920).
[36] VOSBURGH and EPPLEY, *J. Am. Chem. Soc.*, **45**, 10, 2275 (1923).
[37] Paper read at ninth general meeting of the Am. Electrochem. Soc., May 2, 1906.

gam pole gave a constant value of 1.01837 volts at 25°. (The value for a cadmium cell is given as 1.0186 at 20° by Jaeger in "Die Normalelemente," published in 1902. Applying his temperature-coefficient of roughly –.000038, the value for a cell at 25° would be 1.01841.)

Hulett then for thirteen hours rotated a tube, as above, filled with mercury, mercurous sulphate, and saturated cadmium sulphate solution with excess of cadmium sulphate crystals. Upon testing the e.m.f. it was found to be 1.01764 volts, decreasing upon standing. This inconstancy, according to the author, was due to the "mercury being in a finely divided state," the tube having been rotated too rapidly. The tube was therefore rotated slowly, so that the mercury might coalesce to one large globule. Under this treatment the value against the test electrode rose until after twenty-one days the value 1.01990 volts was reached with the value still changing. This is .00140 volt higher than the value of the standard cell.

In the month of August of the same year,[38] Hulett described a similar experiment in greater detail.

In this, after rotating for twelve hours, the value was higher after the system had been at rest three minutes, than it was after it had been at rest three hours (1.0190 volts against 1.0177 volts). The system then was rotated for three days. The value after remaining at rest for five minutes was to all intents the same as that after five hours (1.01938 volts against 1.01941 volts).

Another period of rotation brought the total duration to eleven days. After three minutes of rest, the e.m.f. was 1.01820 volts, after three hours 1.01971 volts, and at the end of twenty-four hours the same. Some clear solution was removed and placed in a tube with mercury, and the system tested with the cadmium test electrode. The value observed was 1.01983 volts.

Rotation was resumed for six and one-half days, the total being seventeen and one-half days. Three minutes after coming to rest, the e.m.f. was 1.01920 volts, and thirty minutes after it was 1.01991 volts, the highest value reached during this "rest-period." Seventy-two hours after, it was 1.01974 volts. The clear solution when tested as above gave 1.01992 volts.

Eight and a half more days of rotation brought the total number of days up to twenty-six. Here the e.m.f. after three

[38] HULETT, *Phys. Rev.*, **23**, 166 (1906).

minutes of rest was 1.0120 volts, increasing to 1.01971 volts seven hours after rotation was stopped, and falling to 1.01943 volts after 170 hours of quiet.

The tube, after standing a week, was spun in a manner that gave the lower (mercury) end a rotary motion which broke the mercury into smaller globules, but did not mix the entire contents of the tube. Two minutes after shaking the e.m.f. was 1.0135 volts, the value rising to 1.01985 volts one hour after the disturbance.

A final test was made by rotating the tube at a rate of one turn in six seconds for three and a half days, and then reducing the rate to one revolution in seventy seconds for one day, "to allow the mercury to collect in one globule." Two minutes after stopping, the e.m.f. against the test electrode was 1.01977 volts, ten minutes after, 1.01978 volts and twenty-four hours after, 1.01964 volts. The clear solution gave 1.01985 volts.

Wolff and Waters [39] repeated Hulett's experiments with modifications. Measurements were made immediately after stopping rotation and raising the holder to a vertical position under the oil in the bath. It is of interest that even when basic cadmium sulphate was added in excess to the cadmium sulphate solution, approximately normal results were obtained from the first, though the paste was quite yellow. Their results, which do not agree with those of Hulett, will be compared with his in detail.

Hulett published another paper [40] in 1908 dealing, among other things, with the equilibrium in rotated mercury-mercurous sulphate-cadmium-sulphate-solution systems to which varying concentrations of sulphuric acid had been added. The mercurous sulphate was pure white and crystalline. Perhaps the most interesting feature of the results was the fact that from a concentration of .810 mole of sulphuric acid per litre to an acid concentration of .08 mole per litre, the mercury concentration in the solution increased uniformly.

In order to determine what rôle mercury played in his rotation experiments, Hulett [41] revolved a tube as before, first without and then with mercury. The mercurous sulphate, perpared chemically, was white and crystalline. The solution of cadmium sul-

[39] WOLFF and WATERS, Bur. Stan. Bull., **4**, 81 (1907–1908).
[40] HULETT, *Trans. Am. Electrochem. Soc.*, **14**, 65 (1908).
[41] HULETT, *Phys. Rev.*, **30**, 5, 648 (1910).

phate must have been neutral, as no mention is made of added acid. After twenty-three and a half hours, the supernatant liquid was tested on a clean mercury surface, against a cadmium amalgam. The e.m.f. was 1.01800 volts, increasing to 1.01870 volts after twelve days, at which value it remained. Mercury was now added to the system and rotation resumed. After seven hours, the e.m.f. was 1.01895 volts, which increased regularly to 1.01955 volts after eighteen days. When electrolytic mercurous sulphate was used, the results were similar, but the initial equilibrium values were not so low and the final values after addition of mercury not so high as in the previous experiment.

The investigator attributes the difference between the mercury concentration in the main body of the solution and that at the mercury surface to a more rapid rate of hydrolysis due to contact with mercury. That the presence of a concentration of sulphuric acid within certain limits maintains a rapidly assumed equilibrium is in accord with the work of Cox, F. E. Smith, Obata, and with the experience in this laboratory.

A consideration of these experiments of Hulett and of Wolff and Waters brings into notice two main facts. The first is that the results of the various rotation experiments of Hulett check each other in principle, and the second that the results of the rotation experiments of Wolff and Waters do not agree at all with those of Hulett.

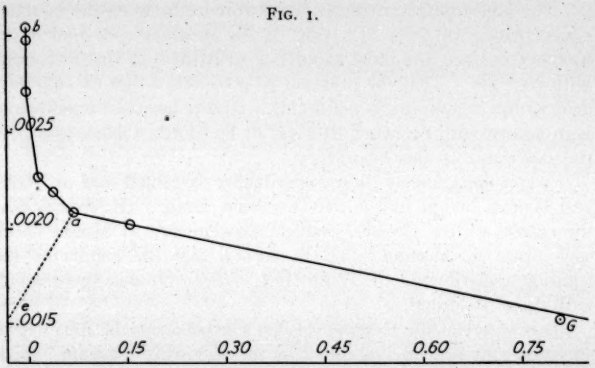
It is worth while to quote Hulett's explanation in full: "The situation may best be illustrated by the following diagram, which gives the concentrations of mercurous mercury in a saturated solution of cadmium sulphate as a function of the varying concentration of sulphuric acid, all at 25°.

"Starting at the point *c*, where the cadmium sulphate solution contains .810 molecular weight of sulphuric acid to a litre, there was found to be .001524 molecular weight of mercurous sulphate in solution when the system was in equilibrium.[42] On decreasing the acid concentration the mercurous sulphate concentration increased uniformly to the point *a*, where the acid concentration was .08 molecular weight in a litre. This line *ac* is an equilibrium curve for this system and represents the solubility of mercurous sulphate in a saturated solution of cadmium sulphate with varying concentrations of sulphuric acid. This curve extends further

[42] *Phys. Rev.*, **27**, 349.

to the right but stops at *a*, along this line the system is made up of mercury and the saturated solution with crystallized cadmium sulphate and normal mercurous sulphate as solid phases. The basic salt cannot exist in this region if the system is in equilibrium. At the point *a*, a distinct break occurs in the solubility curve, for on continuing to decrease the acid concentration the curve *ab* was obtained. A break of this kind in a solubility curve shows that some change has taken place in the nature or number of the solid phases. The change in this system was found to be due to the appearance, at this point, of the basic mercurous sulphate so

FIG. 1.



the point *a* gives the acid concentration at which there may exist in equilibrium, mercurous sulphate, basic mercurous sulphate, cadmium sulphate crystals, mercury, saturated solution and vapor. Now these phases may all result from the four components, cadmium sulphate crystals, mercurous sulphate, water and mercury, therefore at the point *a* we are dealing with a non-variant system, and in order to proceed along the equilibrium curve *ac*, one phase must disappear, and it is the basic salt in this case. Likewise, on taking the system to the left of the point *a*, where the acid concentrations are less than .08, the normal salt must disappear if the system is in equilibrium. Now in all the experiments made with the system in this region, the normal salt was always present in large excess, so the curve *ab* could not have been an equilibrium

curve, but represented the results obtained by rotating such systems until no further changes were observed. If these systems had come to equilibrium they would all have arrived at the point *a*, since there was always more than enough normal mercurous sulphate present to generate the necessary .08 molecular concentration of sulphuric acid. The reason they did not come to equilibrium is due to the slow rate of hydrolysis. When we do have the system in equilibrium in this region—from zero to .08 molecular concentration of sulphuric acid—only the basic mercurous sulphate can be present, and since this has only a small solubility the equilibrium curve here would be something like the dotted line *ae*, which would represent the solubility of basic mercurous sulphate in a saturated cadmium sulphate solution with varying concentrations of sulphuric acid.

"If we cannot bring the cathode system of the Weston standard cell to equilibrium by rotating it, there is, of course, no chance of attaining equilibrium in the cell where the conditions are most unfavorable, but these unfavorable conditions bring about, in a relatively short time, a 'steady state' which is not noticeably affected by ordinary temperature changes, and the result is that most of the Weston standard cells are serviceable for years. They suggest under-cooled liquids or supersaturated solutions, as now and then a cell will slowly decrease to low and indefinite values, while others made at the same time and in the same way do not."

Now, the phase rule defines the conditions under which certain components and phases in contact will co-exist in equilibrium. The rule obviously can be expected to apply, therefore, only when these *are* in contact with each other.

Hence Hulett's reasoning is valid only when applied to the region where all the phases he mentions are in contact, namely, at the surface of the mercury electrode. In his experiments, in order to simulate the conditions in a cell, he took pains to limit the co-existence of these phases to this restricted area, while in the main body of his rotation-tube he had a different system, namely, the system he describes above with mercury omitted, for by design he used white mercurous sulphate. Thus he probably had two sets of transformations taking place simultaneously in different parts of the same tube due to lack of thorough mixing

and the relatively small area of his mercury surface. Therefore the equilibrium he was investigating, that of the system, normal mercurous sulphate, basic mercurous sulphate, cadmium sulphate crystals, mercury, saturated solution and vapor, was upset by entry into it, due to the rotation or to diffusion, of the products of the transformation of another quite different system. This later consisted initially of mercurous sulphate, cadmium sulphate crystals, cadmium sulphate solution and vapor.

Wolff, on the other hand, rotated in a manner "insuring a thorough stirring of the paste and mercury with the electrolyte." He used gray mercurous sulphate as well as white. His results he states in the following words: "It will be seen that no initial low values, as observed by Hulett, were obtained. The Weston cells with gray samples of mercurous sulphate show changes which do not exceed 0.01 per cent., even after continuing the rotation for months . . . The white samples generally showed considerably larger effects, but not as great as those observed by Hulett. There was also a tendency to reach a maximum value, and then, on further rotation, to approach the normal."

In his experiments, Wolff reproduced only the conditions existing at the mercury face of a cell, while Hulett emphasized those evidently found throughout the mass of the depolarizer—these being in force to a greater extent in a white mercurous sulphate, and to a lesser extent in a sulphate which is gray, due to finely divided mercury. His results are another piece of evidence in favor of the belief that in a cell originally neutral, equilibrium will not be established until a certain concentration of acid is provided by the transformation of normal mercurous sulphate into the basic salt, with the attendant formation of sulphuric acid. Wolff and Waters show, by evidence outside of, and in addition to, that provided by standard cells themselves, that reactions can take place at the mercury face that will bring about equilibrium at the point where the e.m.f. is determined.

However, it would seem safest to assist the establishment of this equilibrium by the addition of acid to the electrolyte before it is introduced into the cell.

The usual technique in preparing the mercurous sulphate paste is to transfer the required quantity of the salt to a Gooch crucible, and to wash by suction with cadmium sulphate solution, or with

alcohol and ether.[43] It is probable that this treatment may cause some oxidation to the higher mercuric state.[44]

Vosburgh,[45] therefore, prepared normal cells in which the mercurous sulphate was washed and transferred to the cell vessel with rigorous precautions against oxidation. He found that, if such precautions were taken, neutral cells could be made having a normal value which remained constant.

I quote from his article: "In preparing a series of cells with cadmium sulphate solutions containing various concentrations of sulphuric acid, it was found that the procedure described for protecting the mercurous sulphate from the air was necessary when the acid concentration was below 0.01 mole per litre and desirable up to 0.02 mole per litre. Above that point, however, no trouble was experienced in preparing constant cells by the procedure of Wolff and Waters." (Note: The cadmium sulphate solution was evacuated to expel air. The mercurous sulphate was washed and transferred to the cell under nitrogen, and the air in the cell vessel expelled with nitrogen before hermetically sealing.)

"Cells made with neutral cadmium sulphate solutions were the hardest to prepare in such a manner that they would be constant. A number were prepared as described above, except that the cadmium sulphate solution was not evacuated. Some of them started with initial values as much as 30 to 40 microvolts too high, but decreased rapidly at first until after a month the cells were in good agreement as compared with cells made without special precautions to exclude mercuric ion and were much more nearly constant. They were, however, more variable than cells made with slightly acid electrolytes . . ."

"Although the cells were better than cells made without special precautions against mercuric ion, they were distinctly inferior as regards constancy to cells with acid electrolytes . . ."

With respect to the effect of acid upon the value of the e.m.f., Hulett[46] holds that although the electromotive force is decreased proportionally to the concentration by acid when present in con-

[43] WOLFF and WATERS, Bur. Stan. Bull., **4**, 29 (1907–1908).

[44] Report of work of the Physikal-Techniche Reichsanst, during 1909, *Z. Electrochem.*, **17**, 34 (1910). Report to International Committee on Elect. Units and Standards, Wash. Gov't Printing Office, 1912, p. 111.

[45] VOSBURGH, *J. Am. Chem. Soc.*, **47**, 1258 (1925).

[46] HULETT, *Phys. Rev.*, **27**, 352 (1908).

centrations greater than 0.1 molar, "the linear function applies only for concentrations greater than 0.1 molar acid, since for very small acid concentrations the e.m.f. curve changes are very great and follow quite different curves . . ."

Obata [47] has carried the relationship between acidity and e.m.f. down to 0.04 molar. This he expresses as

$$e = 85.5x$$

where e is the decrease in voltage expressed in 10^{-5} volts, and x the acidity of the electrolyte expressed in terms of normal acidity.

Vosburgh,[48] by means of the neutral cells above, has carried the relationship from .08 molar to neutrality, and finds no large deviation from Obata's relation even at the lowest acidities.

Cox [49] has found that below an acid concentration of 0.0021 molar, mercurous sulphate is transformed to the basic sulphate $2Hg_2O.SO_3$. With this in consideration and in view of the rotation experiments of Hulett, it would seem reasonable that the conditions at the mercury surface which fix the e.m.f. may not have existed elsewhere in the depolarizer in the neutral cells made by Vosburgh; that is, the equilibrium is a local one maintained by the prevention of diffusion from the mercury surface by the overlying mercurous sulphate.

The relation of electromotive force to cadmium sulphate concentrations in the electrolyte of unsaturated cells is of practical interest. We [50] have found that the electromotive force of a series of forty-five unsaturated Weston cells increased in an approximately linear manner as the cadmium sulphate concentration decreased.

The temperature-coefficient of a normal cadmium cell is the algebraic sum of the coefficients of the two electrodes, for F. E. Smith [51] has determined that of the mercurous sulphate limb alone at 20° to be 0.00031 volt for a temperature-rise of 1°, and that of the cadmium limb alone to be −0.00035 volt for an equal change. The difference between these two is practically identical with the value found by Wolff below.

[47] OBATA, *Proc. Math. Phys. Soc.*, Japan (3) **2**, 235 (1920).
[48] VOSBURGH, *J. Am. Chem. Soc.*, **47**, 1265 (1925).
[49] COX, *Zeit. anorg. Chem.*, **40**, 180 (1904).
[50] VOSBURGH and EPPLEY, *J. Am. Chem. Soc.*, **45**, 2276 (1923).
[51] F. E. SMITH, *Phys. Soc. Proc.*, **22** (1910).

Dearlove [52] investigated the temperature-coefficient of several lots of cells. However, they must have differed so from modern normal standards, because of differences in their methods of preparation, that his results can have little more than historical interest.

Wolff [53] expresses the temperature-electromotive force relationship of normal cells, with neutral electrolyte (or at least with no added acid), made without specific care to exclude mercuric ion, within the range 0°–40°, by the formula

$$E_t = E_{20} - .0004075\ (t-20) - .000000944\ (t-20)^2 + .0000000098\ (t-20)^3.$$

This formula superceded that of Jaeger and Wachsmuth [54] from which it differed appreciably. It has been criticized by Cohen and Wolters,[55] and by Steinwehr,[56] because it predicts a solubility minimum for hydrated cadmium sulphate at 3°, while the most reliable data on this solubility indicate a minimum in the vicinity of −9°. The formula of Jaeger and Wachsmuth predicts a minimum at this temperature, based, however, upon an extrapolation. Wolff's formula has been accepted as the international standard since 1908.

Obata [57] measured the temperature coefficients between 15° and 30° of four cells with electrolytes containing from 0.04 to 0.38 mole of sulphuric acid per litre. He found that the coefficients increased with the acidity, and that each had a temperature-coefficient larger than the neutral cell.

Vosburgh and Eppley [58] determined the electromotive forces of three lots of five cells each at 15.00°, 24.98°, 35.03°, 40.03° and 45.04°. A differently prepared sample of mercurous sulphate was used in each lot. All cells had the same electrolyte containing 0.012 mole of sulphuric acid per litre. The agreement among these cells was excellent.[59] The agreement with the corresponding values calculated by Wolff's formula for the first four tem-

[52] DEARLOVE, *Electrician*, **31**, 645 (1893).

[53] WOLFF, Bur. Stan. Bull., **5**, 326 (1908).

[54] JAEGER and WACHSMUTH, *Ann. Physik.*, **59**, 575 (1896); *Wied Ann.*, **59**, 575 (1896).

[55] COHEN and WOLTERS, *Verschlag. Akad. Wettenschappen Amsterdam*, **26**, 795 (1918); *Zeit. phys. Chem.*, **96**, 257 (1920).

[56] STEINWEHR, *Zeit. phys. Chem.*, **94**, 14 (1920).

[57] OBATA, *Proc. Math. Phys. Soc.*, Japan, **2**, 235 (1920).

[58] VOSBURGH and EPPLEY, *J. Am. Chem. Soc.*, **45**, 2272 (1923).

[59] The average variation from the group average was 2.5 microvolts.

peratures, the range of the formula, was well within 0.001 per cent., Wolff's values being higher.

The same two authors [60] observed the electromotive forces of a series of cells, the electrolyte of which was 0.02 normal with respect to sulphuric acid, at 25° and 35°. The observed voltages were on the average about 5 microvolts lower than the values calculated by Wolff's formula. The mercurous sulphate varied within wide limits as to grain-size, and various methods of preparation of the salt also had been used. The difference between the electromotive forces at 25° and 35°, respectively, was independent of the mercurous sulphate preparation.

Vosburgh, in a paper that it is hoped will soon be published, gives the results of a determination of the temperature-coefficients of twelve neutral cells set up with the precautions to exclude the introduction of mercuric ion through oxidation, already noted. They agreed to a few microvolts with the calculated values.

It must be emphasized, however, that a constant electromotive force at the various temperatures was attained only after the elapse of two weeks in the case of many of the cells.

The temperature-coefficient of the unsaturated cell is usually spoken of as being "negligible." Upon those certificates of cells furnished by the Weston Electrical Instrument Company which I have seen it was given as "less than −.00001 volt per degree C." In the unsaturated cell the electrolyte is supposed to be saturated with cadmium sulphate at 4° C.

We [61] have investigated the relationship between the degree of saturation of the solution and the e.m.f. as well as the resulting temperature-coefficient, in unsaturated cells having an electrolyte 0.012 molar with sulphuric acid. We found that a cell with an electrolyte containing 42.93 per cent. cadmium sulphate should have a zero temperature-coefficient between 15° and 35°. In such a cell the solution would be saturated at about 4°.

Four groups of "neutral" unsaturated cells also were measured at 25° and 35°. They were prepared with an electrolyte made by neutralizing four of the acid solutions of cadmium sulphate used in the cells above by means of cadmium oxide. Their temperature-coefficients when plotted against e.m.f. lay

[60] VOSBURGH and EPPLEY, *J. Am. Chem. Soc.*, **46**, 1, 110 (1924).
[61] VOSBURGH and EPPLEY, *J. Am. Chem. Soc.*, **45**, 10, 2275–77 (1923).

neither on a straight line nor on any regular curve. In these cells no particular pains were taken to exclude mercuric ion.

Our results for the slightly acid cells are summarized as follows:

The electromotive forces were linear functions of the temperatures between 15° and 35°, but were not linear functions between 35° and 45°.

The temperature-coefficient between 15° and 35° was found to be a linear function of the electromotive force. It decreased from 0.0000028 volt per degree for cells with an electromotive force of 1.01827 volts to −0.000013 volt per degree for cells with an electromotive force of 1.0210 volts, being zero for a cell with an electromotive force of 1.01873 volts, these e.m.f.s corresponding to a temperature of 25°.

Vosburgh, in a paper to be presented to the *Journal of the Optical Society of America and Review of Scientific Instruments*, presents the results of measurements of ten cells with 13 per cent. amalgam, and ten cells with 12.5 per cent. amalgam, at 22.2°, 35.0°, 42.0°, 50.0°, 56.0° and 60.0°. They then were measured again at 25.0°. These cells were portable, unsaturated cells with cork and linen septa, having an electrolyte containing about 0.04 mole of sulphuric acid per litre. The cadmium sulphate of the solution was of a concentration corresponding to a saturation somewhat below 4°.

The cells with 13 per cent. amalgam showed no appreciable variation in e.m.f.—that is, a constancy of 0.01 per cent. or better—over the entire range from 22.2° to 60°. There were, however, indications of a minimum in the e.m.f. between 35° and 42°. These indications are so slight as perhaps to be fortuitous. I hope to examine the matter further as soon as opportunity presents itself.

Some of the cells with 12.5 per cent. amalgam showed a drop in e.m.f. at 56°, and a still further drop at 60°. However, cells with 12.5 per cent. amalgam can be used up to about 55° with a degree of accuracy of 0.01 per cent. The behavior of cells under a decrease in temperature will be treated under hysteresis.

In general it may be said that portable unsaturated cells exhibit larger negative temperature-coefficients than non-portable cells of the same electromotive force.[62] Cells of the same group

[62] VOSBURGH and EPPLEY, *J. Opt. Soc. Amer.*, 9, 1, 65 (1924).

do not agree among themselves so well as do portable cells. The differences in the cells examined, though, were of no practical importance, the largest among one group of the cells being –6 microvolts per degree, which would cause a change of .01 per cent. in the value of the voltage for a temperature change of 15°.

Data of F. E. Smith [63] give the electromotive forces of cells with concentrations of cadmium in their amalgams of from 1 per cent. to 20 per cent. at temperatures five degrees apart from 0° to 45°. These figures show that between 9 per cent. and 12.5 per cent. of cadmium and between 0° and 45° temperature, the e.m.f. is the same. Hence, within the "useful range" of cadmium concentrations in the amalgam, the temperature-coefficient is not affected by the per cent. of cadmium. Nevertheless the composition of the amalgam and its treatment have a marked effect upon hysteresis, as will be noted in the discussion of that phenomenon.

A normal cell with negligible temperature-coefficient would be a distinct advance, because of its reproducibility. The systems cadmium-tin-mercury and cadmium-lead-mercury have been investigated by Kremann, Prammer and Helly.[64] They found that the addition of tin or lead to a two-phase cadmium amalgam gave a system that showed a constant potential difference against a solution containing cadmium ion for quantities of the added metal between 10 and 75 atomic per cent. of the whole. Vosburgh [65] has made normal Weston cells in which antimony, tin, lead, copper or bismuth were added to the cadmium amalgam. Antimony did not give reproducible results, while copper made no appreciable difference either at 25° or 35°. The lead amalgam behaved electrically, practically in the same manner as did that of tin, but gave off gas more readily in an acid cadmium sulphate solution than did either tin or bismuth amalgam. Hence only the amalgams of tin and bismuth are of interest from our standpoint.

Cells were made up with slightly acid cadmium sulphate solution, with precautions to exclude mercuric ion. They differed from slightly acid Weston cells only in that the amalgam contained a third metal.

[63] F. E. SMITH, *Nat. Phys. Lab. Coll. Research*, **6**, 137 (1910).

[64] KREMANN, PRAMMER and HELLY, *Z. anorg. allgem. Chem.*, **127**, 295 (1923).

[65] VOSBURGH, *J. Am. Chem. Soc.*, **47**, 2531 (1925).

The components of the tin-cadmium amalgams were present in the following proportions, the same being expressed in atomic per cent.:

	Sn	Cd	Hg
(1)	14.9	14.1	71.0
(2)	13.1	14.3	72.6
(3)	11.9	15.4	72.7
(4)	10.7	15.7	73.6

The tin cell at 25° showed an e.m.f. of 1.019005 volts. Duplicate cells agreed within 5 microvolts.

After equilibrium was assured at 25°, the electromotive forces were measured at 20°, 15°, 20°, 25°, 30°, 35°, 40°, 35°, 30°, and finally at 25°. Practically no hysteresis was observed, although the temperature was maintained constant for at least four days after a rise, and for at least two weeks after a fall in temperature. The e.m.f. at 40° was 0.00056 volt lower than at 15°, giving an average temperature-coefficient of 0.00002 volt per degree. The relation between electromotive force and temperature of the cell with the cadmium-tin amalgam anode is

$$E_t = E_{25} - 0.0000205\ (t-25) - 0.00000043\ (t-25)^2 + 0.000000008\ (t-25)^3.$$

Some cells were set up with the three-metal amalgam for one pole and the standard cadmium amalgam for the other, the electrolyte being that of the Weston cell with excess of cadmium sulphate crystals. In these cells the cadmium amalgam without the third metal was the positive pole. Their e.m.f. was 0.0009550 volt at 25° for the first three amalgams listed.

Since the cathode of this amalgam cell is identical with the anode of the Weston, an amalgam cell in series with a Weston cell should give an electromotive force of

$$1.018046 - 0.000955 = 1.019001 \text{ volts.}$$

This is within 4 microvolts of the observed value. This condition holds with the same accuracy from 15° to 40°. It indicates that the third metal merely increases the activity of the cadmium.

Bismuth behaved much as did tin—or lead with the exception of the evolution of gas—but the electromotive force and temperature-coefficient were both larger. The constant potential range for amalgams with bismuth as the third metal is from about 5 atomic per cent. to about 20 atomic per cent., the cadmium and mercury being present in from one to nine parts by weight.

The determination of temperature-coefficients brings out the fact that many cadmium cells do not come quickly to a steady state when their temperature is changed. Wolff,[66] discussing results of previous investigators who determined temperature-coefficients, says that Barnes[67] found large differences in the values of four cells rapidly brought from 15° to 0°. Barnes states, with respect to three other cells, that under 15° no regularity can be said to exist. Wolff says that certain discrepancies in Jaeger's[68] work seem to be due to hysteresis. Both of the above investigators made use of a 1 : 6 amalgam.

Wolff himself discarded from his calculation of the temperature-coefficient the results of sixty-three out of the 200 cells with which he started, because of hysteresis. He further found in transferring a number of normal cells back and forth from a bath maintained at 25° to one at 20°, that even with "abrupt changes in temperature, most of the cells reached a practically constant value well within an hour, with ascending temperature. On lowering the temperature, a longer time was needed for the attainment of the normal values." Vosburgh[69] found the same conditions to exist.

The research of Bijl[70] established the fact that within certain concentrations of cadmium and within certain temperatures, cadmium amalgam consists of a solid solution of cadmium in mercury (a solid phase) and a solution of this in mercury (a liquid phase). Bijl set the limits of concentration for the temperatures at which these two phases could co-exist. F. E. Smith[71] confirmed these results and further fixed the conditions under which a cadmium amalgam is in equilibrium with a cadmium sulphate solution. He prepared a number of cells in such a form that their amalgams of various cadmium content could be compared with a 10 per cent. amalgam as an opposite pole.

Amalgams containing from 1 to 13.5 per cent. cadmium (excepting the 6 per cent. amalgam) when maintained at a constant temperature were constant to 1 or 2 parts per 100,000. The 6 per cent. amalgam at 30° was inconstant, due to its near-

[66] WOLFF, Bur. Stan. Bull., **5**, 2, 313 (1908).
[67] BARNES, *Jour. Phys. Chem.*, **4**, 339 (1900).
[68] JAEGER, *Ann. d. phys.*, **4**, 123 (1901).
[69] VOSBURGH, "Applicability of Wolff, Temp. Formula," *J. Opt. Soc. Am.*
[70] BIJL, *Zeit. phys. Chem.*, **41**, 641 (1902).
[71] F. E. SMITH, *Proc. Phys. Soc.*, **22**, 139 (1910).

ness to the temperature (28°) at which its two-phase system goes over into a liquid single-phase system. The transition is a slow one, seemingly, and the cell does not assume immediately a constant value.

Many of his cells containing 14 per cent. to 20 per cent. cadmium were not constant even when the temperature was unchanged, as was shown when cells were kept at 15° for three months. During this time the 15 per cent., 17 per cent. and 19 per cent. amalgams fell in e.m.f. and those with 14 per cent., 14½ per cent. and 16 per cent. cadmium rose in value. Excepting the 18 per cent. and 19 per cent. cells, which fell in e.m.f., there was very little change at higher temperatures. Smith says that cells containing from 2 to 11.5 per cent. cadmium are constant. Amalgam cells containing 12 to 13.5 per cent. showed drops of a few hundred-thousandths of a volt, and those still richer in cadmium (excepting the 20 per cent. amalgam) showed changes which in two cases (14.5 and 16 per cent.) equalled 0.004 volt, when kept in cracked ice for six weeks.

Amalgams of higher cadmium content than 11 per cent. showed abnormal equilibrium results when melted and chilled suddenly below their freezing-points. No difference greater than two hundred-thousandths of a volt was seen between the e.m.f. of chilled and slowly cooled amalgams of the same concentration in the range 1 per cent. to 11 per cent. Heating even to 45° made a 14.5 per cent. amalgam behave at 0° like one of 13.5 per cent. According to Smith, the effect of heating to a temperature below the melting-point of the particular amalgam and then allowing it to cool slowly is to coat the solid grains of the amalgam with a layer of lower cadmium concentration deposited from the liquid phase. The concentration of this is smaller than that normally corresponding to temperatures below the point to which the amalgam was heated. Diffusion, in time, makes the whole grain of the same cadmium content throughout, but until this is completed, abnormal values result.

Since, when amalgams of the same cadmium content were melted and chilled, the cells of which they were components did not agree in e.m.f. even after the lapse of several weeks, the effect of chilling cannot be a simple one. Smith recommends a 10 per cent. amalgam as best between 0° and 51°. Cohen and Krupt [72] recommend one of 8 per cent.

[72] COHEN and MOESVELD, *Zeit. phys. Chem.*, **95**, 3, 304 (1920).

Wolff and Waters [73] call attention to the hysteresis caused by coarse-grained mercurous sulphate, due to the small surface exposed to the solvent action of the electrolyte, a phase of the problem shown also by Steinwehr [74] to require attention.

Wolff and Waters [75] opened on December 19, 1906, three cells that had been rotated, and used the paste from them to set up cells of the ordinary form. One cell had gray sulphate, the other two, white. The gray sulphate cell had practically the normal value after two days. The two cells with white mercurous sulphate showed values 600 mmv. and 400 mmv., respectively, higher than the normal, decreasing until March 25, 1907, on which date they were transferred from the bath in which they had been maintained at 25° to one at 20°. The two cells showed marked hysteresis, which persisted with slight changes for a long time. Wolff suggests that either a surface film had formed on the crystals during rotation, or a large excess of cadmium sulphate was used in the paste, by this means retarding the establishment of saturation with the depolarizer. Wold [76] described an hysteresis due to a lag in the solution or precipitation of cadmium sulphate. This would appear only in normal cells.

That cells having about 0.05 gm. of asbestos per cell, mixed with the mercurous sulphate, have an hysteresis slightly greater than those without asbestos, is noted by Vosburgh and Eppley.[77]

Neutral unsaturated cells without septa show large hysteresis. Neutral cells with septa show even more. Cells without septa with an acid concentration about .012 mole per litre, show very little hysteresis when made with an average grain-size of mercurous sulphate. Portable cells (cells with septa) showed a very appreciable hysteresis (of the order of 0.1 per cent. of the value of the cell) with this concentration of acid in the electrolyte. When the temperature fell the electromotive force rose to an abnormally high value, and decreased slowly, sometimes requiring over a month to attain a constant value again. It is interesting that in newly made cells the hysteresis is generally low and increases during the first few months.

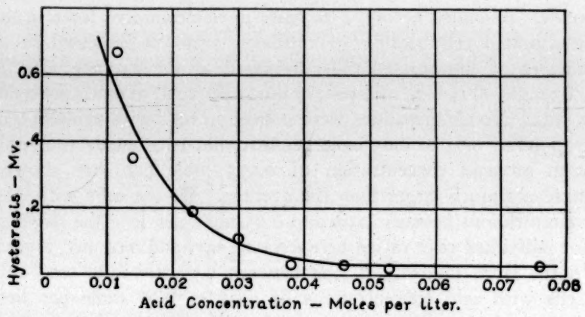
Cells show relatively much less hysteresis when the tempera-

[73] WOLFF and WATERS, Bur. Stan. Bull., **4**, 71 (1907–1908).
[74] STEINWEHR, *Zeit. Elektrochem.*, **12**, 578 (1906).
[75] WOLFF, Bur. Stan. Bull., **4**, 87 (1907–1908)
[76] WOLD, *Phys. Rev.*, **27**, 329 (1908).
[77] VOSBURGH and EPPLEY, *J. Opt. Soc. Amer.*, **9**, 1, 72, 1924.

ture is changed from 25° to 35° than they show when brought from equilibrium at 35° to 25°.

When cells with the abnormal e.m.f. resulting from a temperature drop are brought back to the higher temperature at which they were in equilibrium, as indicated by a constant e.m.f. in agreement with that considered standard, this normal value is almost immediately assured. While it is not safe to attempt a

FIG. 2.



detailed explanation of this phenomenon in the absence of complete data, it is possible that upon a rise in temperature, equilibrium is established by a reaction in solution, and upon a drop, by the transformation of a solid—formed in solution at the higher temperature, and deposited out due to decreased solubility in the lower temperature range. The first reaction would be rapid, the second slow.

Acid in portable cells reduced the hysteresis to very small proportions. Such cells having from 0.04 mole of sulphuric acid per litre up showed very slight hysteresis, the hysteresis changing little, if any, from 0.04 mole per litre to 0.76 mole per litre, this latter concentration being the upper limit of the range investigated. The hysteresis for a 0.03 molar electrolyte with respect to sulphuric acid was about twice that for one 0.04 molar. However, when a very finely divided mercurous sulphate was used, in which there was much finely divided mercury, an acidity of 0.03 mole per litre reduced the hysteresis to nearly zero.

In 1910, as a result of some eighty-three values obtained with the silver voltameter, the delegates to the International Technical Committee recommended to the International Committee on Elec-

trical Units and Standards that the value of the Weston normal cell be fixed at 1.0183 international volts at 20° C. While slight differences as to the weights to be given different determinations arose, these could not affect the final result by as much as 1 part in 10,000.[78] This value is now internationally accepted.

Cells set up by the leading national standardizing laboratories do not differ more than 1 part in 100,000.[79]

The constancy of a standard cell is an important thing to know. As stated before, a decrease in electromotive force in the unsaturated cell because of diffusion is to be expected.[80] A number of unsaturated cells decreased at the average rate of 0.03 millivolt to 0.04 millivolt, or 0.003 per cent. to 0.004 per cent., a year. No abnormalities were noticed in cells with acid concentrations of 0.03 to 0.05 mole per litre, but two out of four cells with an acid concentration of 0.075 mole per litre showed decreases much larger than the average. Of the cells with acid concentrations between 0.03 and 0.05 mole per litre the decrease for individual cells varied between 0.01 mv. and 0.07 mv. a year. In the large majority it was between 0.02 mv. and 0.05 mv. Cells with acid concentrations of 0.01 to 0.02 mole per litre showed abnormalities, a group of such cells showing a much greater decrease than others, and the agreement between the individual cells of the group being very poor.

With normal cells, it has been my experience that the value will remain constant within 10 microvolts for long periods of time, say at least five years, if the cells are acid. Two cells made in 1916 show a drop to date of 20 microvolts and 30 microvolts, respectively. The average of the cells of the Bureau of Standards shows no marked differences against the value of similar freshly prepared cells sent there for comparison. I understand that most of the Bureau cells were made in 1912, so from this some idea of the dependability of the cadmium cell can be obtained. As remarked by Shaw and Reilley,[81] "the constancy of such cells is equal to that of good resistance coils . . ."

[78] Suppl. to Report to International Committee on Elec. Units, Gov't Printing Office, p. 5 (1912).

[79] WOLFF and WATERS, Bur. Stan. Bull., **4**, 80 (1907–1908). OBATA, *Proc. Tokyo Math. Phys. Soc.*, **2**, 9, 321 (1918).

[80] VOSBURGH, *J. Opt. Soc. Amer.*, **11**, 1, 59 (1925).

[81] SHAW and REILLEY, *Trans. Roy. Soc. Canada*, 13, Sect. 3, 171 (1919).

POSITIVE RAYS PRODUCED IN THERMIONIC VACUUM TUBES CONTAINING ALKALI-METAL VAPORS.*

BY

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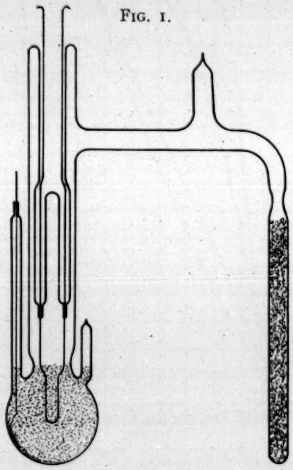
IN THE course of a study of the influence of temperature on the photo-electric effect of the alkali metals,[1] an influence which was ascribed to a variation of the work function with temperature, an independent measure of the inferred variation of work func-

FIG. 1.



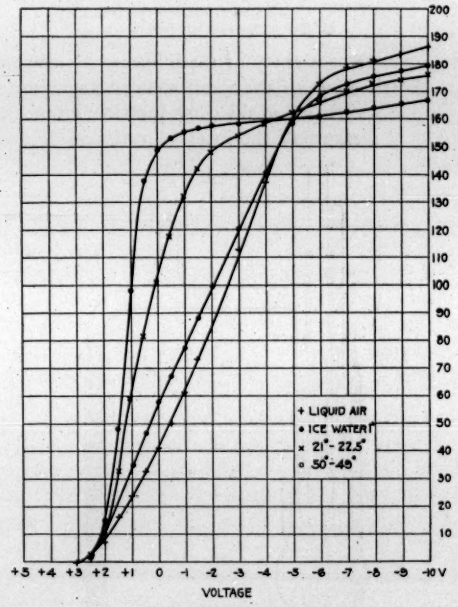
Thermionic vacuum tube with alkali-metal-covered walls.

tion was sought by investigating the voltage-current relation in thermionic emission. For this purpose a tungsten filament was mounted in the middle of an evacuated bulb, the walls of which were covered with potassium. (Fig. 1.) Voltage-current curves were then obtained with the bulb at room temperature and at the

* Communicated by the Author.

temperature of liquid air. In accordance with well-established principles, it was anticipated that the voltage-current curve would be bodily shifted parallel to itself by the amount of the variation in work function, as expressed in volts. Such a shift was in fact found,[2] and in the direction expected. On carrying the work further, however, it developed that the alteration of the voltage-

FIG. 2.

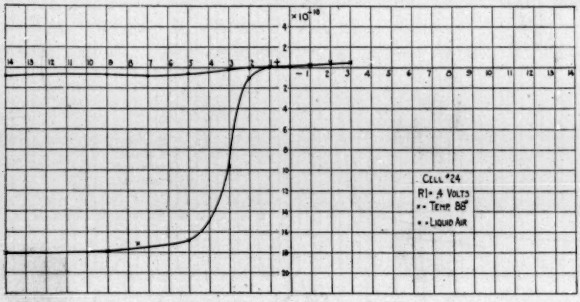


Voltage-current curves obtained with a thermionic tube containing potassium vapor at various temperatures.

current curve did not consist of a simple shift of the curve along the axis of voltages, but in a change in the shape of the curve as well. A typical example of the change in the thermionic voltage-current curve as produced in a cell of the type described, when the temperature of the bulb is varied, is shown in Fig. 2, obtained with a cell containing potassium. The voltage-current curve obtained when the bulb is immersed in liquid air, thereby con-

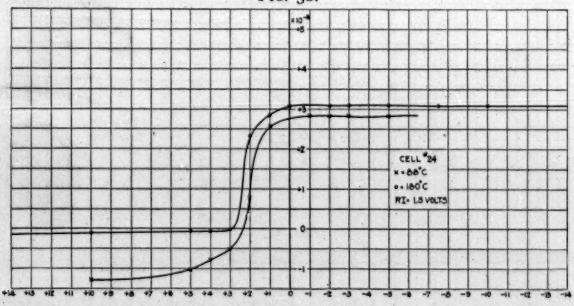
densing the alkali-metal vapor, may be considered as typical of a high vacuum cell. (Owing to the contact potential difference between tungsten and potassium the curve extends considerably farther toward positive voltages than with ordinary thermionic

FIG. 3a.



Voltage-current curves obtained with a thermionic tube containing sodium, showing negative and positive currents at high and low temperatures of the alkali-metal vapor and for various filament temperatures.

FIG. 3b.



tubes.) As the cell temperature is raised the current rises much quicker to saturation than in a vacuum cell.

This change in the character of the saturation curve is similar to the change which has been known for some time to occur in the presence of mercury vapor,[3] because of the ionization of the mercury vapor, whereby positive ions are produced. These reduce the space charge due to the emitted electrons, and so permit quicker saturation. It appeared probable, therefore, that the

FIG. 3c.

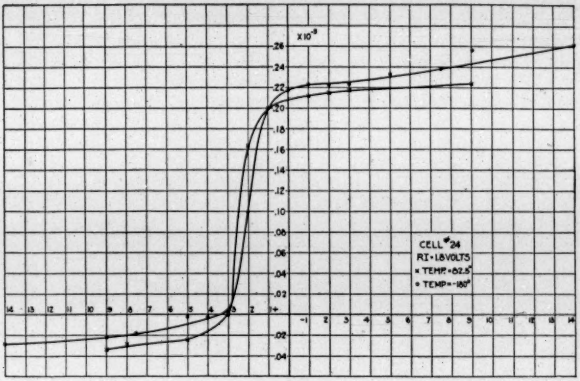


FIG. 3d.

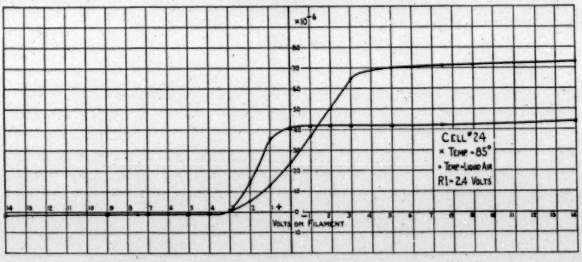
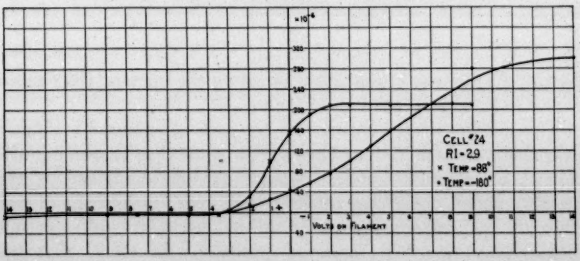
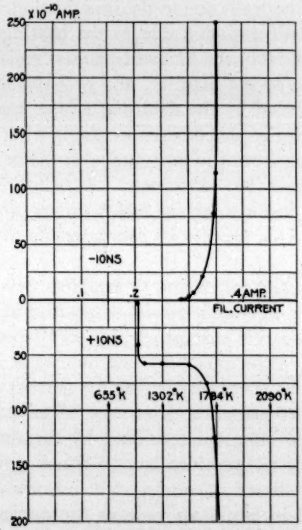


FIG. 3e.



effect in the present case was due to the presence of positive ions of alkali metal. These positive ions, however, differ from the ions produced in mercury vapor in several respects. For one thing, they appear even when the potential difference within the tube is inferior to the ionizing potential of the alkali-metal atoms. A still more striking difference, however, is the fact that these positive ions may be obtained even when there are no electrons present at all. This phenomenon is shown by the family of

FIG. 4.



Positive and negative currents as a function of filament temperature. (Sodium vapor.)

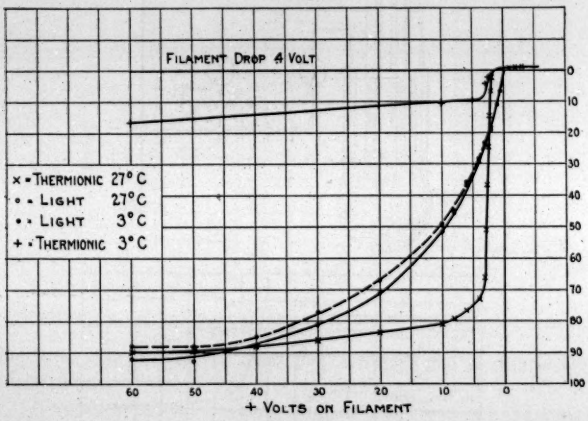
voltage-current curves exhibited in Fig. 3, where the filament temperature is varied over a considerable range, and the voltage-current curves are obtained for both room and liquid-air temperatures of the bulb. It will be seen that for low temperatures of the filament, the only current obtained is a positive current from the filament to the walls. This is shown also by the curves of Fig. 4, in which positive and negative currents are plotted against heating currents through the tungsten filament. At low filament

temperatures the only current present is the positive current. As the filament temperature is raised, a region is attained where the tungsten filament begins to emit electrons, due to its high temperature. At about the same temperature, the positive current, which has been fairly constant over a considerable filament-temperature range, begins to rise. The positive current, which occurs in the temperature range where the filament is emitting electrons and which increases with filament temperature, appears to be a mixture of several effects, in some part, photo-electric emission from the walls due to the illumination from the filament, in part thermionic emission due to the heating of the cell walls by the radiation from the filament, in part emission due to alkali metal boiled out of the filament, and probably its character is, in part, also influenced by the field due to the presence of negative electrons. With the phenomena occurring after the beginning of electron emission from the clean tungsten filament, we shall not in the present paper be concerned. *Attention will be focussed entirely on the positive current which occurs when the filament is at a temperature too low for its characteristic thermionic emission to occur.*

It is, of course, important to establish beyond question that this current does, as stated, consist of positive ions of alkali metal, and not of a negative current of any sort from the walls of the vessel. Several experiments to test this point will be described. The most obvious possibility is that the current is really a reverse current of photo-electrons from the alkali-metal-coated walls. This is rendered improbable at once by the very great influence which change of temperature has on the magnitude of this current. Thus, as shown in certain of the curves of Fig. 3, immersion of the cell in liquid air reduces the current to a negligible fraction of its value. While, as shown in other papers,[1] the photo-electric current from the alkali metals is decreased by a decrease of temperature, the change in magnitude here shown is altogether too large to be ascribed to this effect. A second test of this possibility is furnished by considering the shape of the voltage-current curves for the positive emission. In Fig. 5 is shown (lowest curve) a voltage-current curve for the positive current from potassium; it shows a very quick and thorough saturation at low voltages. This would be characteristic of the

structure employed, in which the filament is of small dimensions as compared with the walls, provided the current carriers flow from the filament to the walls. In the same figure is shown the voltage-current curve for the photo-electric emission from the walls as produced by illumination from an external source. It will be seen that the saturation is poor, as is to be expected of particles coming from the large walls to the small filament. It may be noted at the same time that the illumination necessary to produce the photo-electric current of the same order of magnitude as the positive current was many times greater than that due

FIG. 5.



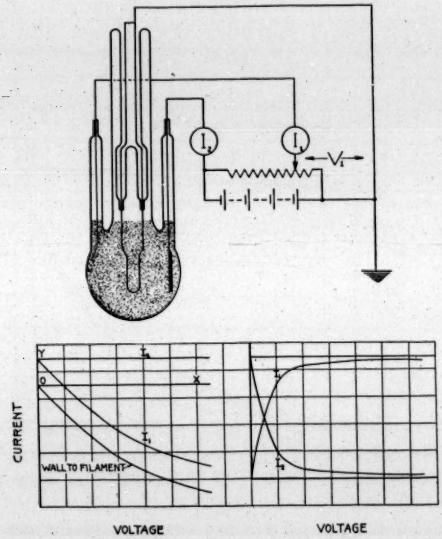
Positive ion and photo-electric currents, compared for saturation and for variation with temperature of bulb.

to the filament, which in this case was raised merely to a dull, red glow. This same set of curves also confirms the conclusions drawn for the effect of temperature. The photo-electric current is only slightly affected by the 24° change of temperature, the positive current is reduced to one-sixth value.

Another experiment may be described in some detail. A special tube was constructed in which, in addition to the tungsten filament and the coating of potassium on the walls, a third electrode was inserted, consisting of a small plate standing between the filament and the tube wall. This cell was connected in the

manner shown in the diagram (Fig. 6). If the current observed is due to electrons from the walls, however produced, it is to be expected, as the voltage between the filament and bulb wall is raised, that the current through the galvanometer in series with the bulb wall will flow first one way and then the other, in the manner shown in the lower left-hand diagram. The current from the inserted plate should at the same time maintain a fairly con-

FIG. 6.



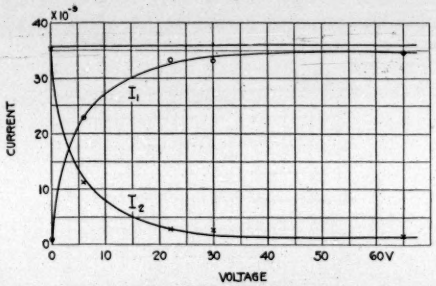
Special cell with auxiliary electrode, and hypothetical voltage-current relations on two different assumptions as to origin of positive current.

stant value; the electrons merely shifting their distribution between the bulb wall and the filament as the voltage changes. On the other hand, if the current is due to positive particles emitted from the filament, we should look for a uniform shift of the stream from the inserted plate over to the bulb as the voltage is increased, and would expect the currents to bulb and plate always to be complementary in value, as shown in the lower right-hand diagram of Fig. 6. The results of trying this experi-

ment are shown in Fig. 7, and are seen to agree entirely with the hypothesis that positive particles flow from the filament, and to disagree with the alternative hypothesis.

A further test is afforded by determining the mass of the carriers of the current. This may be done by finding, in a tube with coaxial cylindrical electrodes, the slope of the voltage-current curve when plotted on coördinate paper where the ordinates (current) are proportional to the two-thirds power of the current. The results of such plotting will be described more in detail later in the paper. It will suffice for the present to state that in a typical case, namely, cæsium vapor considerably above room temperature,

FIG. 7.



Observed distribution of current between walls and auxiliary electrode, as potential difference is varied between wall and filament.

the ratio e/m indicates a mass 133, which is the atomic weight of cæsium.

An additional experiment, which is also given here in anticipation of its fuller description later, is the application of a strong magnetic field to a tube with coaxial cylindrical electrodes. It is found that a field which suffices to completely block the passage of electrons from the filament to the walls has no effect whatever on the positive current, which is in accord with the idea that the positive carriers are many times larger than the electrons. It is only when filament temperatures are used, such that electrons are normally emitted, that magnetic fields of the order of magnitude mentioned have any effect at all. For low voltages between filament and cylinder the effect of the field is then to remove the electron current, thus increasing the apparent positive current. For higher voltages against which the electrons cannot flow, the effect

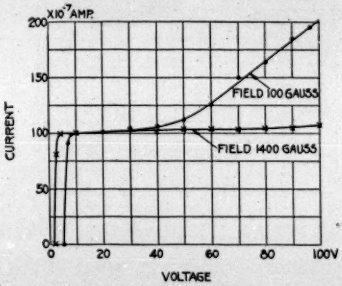
of the magnetic field is to improve the saturation of the voltage-current curve, by preventing the flow of photo and other electrons from the outer electrode (Fig. 8).

These various tests all agree in indicating that we have, under the conditions described, *the production of positive ions of the alkali metals unaccompanied by negatives,* and that these under proper potential gradient give a positive current similar except for the sign of charge and the mass of the particles, to the pure electron current obtained from incandescent metals in high vacuum.

CHARACTERISTICS OF THE POSITIVE CURRENT.

In the course of this study a large number of special thermionic tubes was prepared containing the alkali metals, sodium,

FIG. 8.

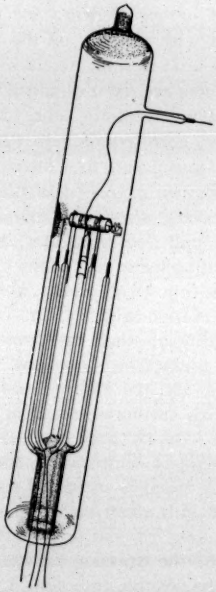


Effect of magnetic field on saturation of apparent positive current when this is mixed with electron current from cell walls.

potassium, rubidium, and cæsium. A typical tube, which embodies practically all of the features necessary for the production of the phenomena under consideration, is shown in Fig. 9. In this tube the pure tungsten filament is a straight wire under slight tension, coaxial with which is a platinum cylinder serving as the other electrode. This cylinder is placed between two other cylinders which serve as guard rings, the galvanometer connections being made to the filament and the centre cylinder. In the tube shown the cylinders and filament are at right angles to the axis of the cylindrical, glass enclosure, a construction adopted with certain of the tubes in order to permit their introduction into a magnetic field. The cells were exhausted to a high vacuum by

means of a mercury diffusion pump, the usual precautions as to baking out the parts being observed. The platinum cylinders were freed of gas by electronic bombardment, and after the introduction by distillation of the carefully purified alkali metals, the filament was operated for a time at the highest safe temperature in order to insure the freeing of its surface from oxides or

FIG. 9.



Special thermionic tube containing alkali metal.

other impurity. Charcoal tubes for immersion in liquid air were provided on most of the cells.

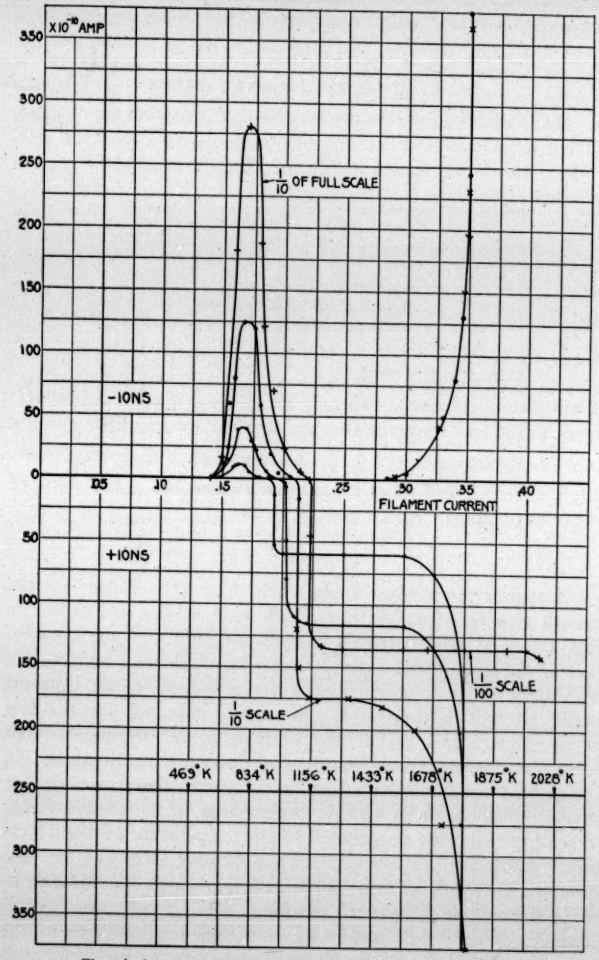
Currents were usually measured by a Leeds and Northrup type H d'Arsonval galvanometer fitted with a series of shunts to vary the sensibility, although with high vapor pressures and correspondingly large currents a micro-ammeter was occasionally employed. In order to avoid disturbing effects due to the voltage drop along the tungsten filament, this was operated by

alternating current through a tungar rectifier commutating device, described elsewhere by Germer,[4] so that the emission measurements were actually made with no voltage drop along the filament. The filament currents indicated on most of the diagrams are the values as read on a d.c. instrument, and, being subject to a correction factor, are only significant as to relative values. Approximate filament temperatures are indicated in certain cases.

A typical set of curves showing the positive and negative currents as obtained with all four of the alkali metals, sodium, potassium, rubidium, and cæsium, is shown in Fig. 10. In this figure, the curves shown are those obtained with a potassium tube for a series of temperatures of the tube, obtained by enclosing it in an electric furnace, corresponding to various pressures of the alkali-metal vapor. Considering first the electronic current, it will be noted that this shows, at very low filament temperatures, a thermionic current which rises with filament temperature, then falls to a low value, and then once more rises and continues to increase with filament temperature. This low-temperature hump, which occurs with all four alkali metals, although it is so small as easily to escape observation with sodium, constitutes the electron emission from a coating of alkali metal on the tungsten filament. When the filament temperature becomes sufficiently high, this coating is driven off, and the electron emission diminishes to a very low value. With further increase in filament temperature, the electron emission from the pure tungsten sets in and continues to increase as the filament temperature rises. When the vapor pressure of the alkali metal is increased the amount of filament permanently covered with alkali metal increases and the coating persists to higher filament temperatures, as is shown by the greater height and breadth of the emission curve.

Taking up now the positive emission, it will be noted that this begins quite abruptly, at a filament temperature which varies with the vapor pressure of the alkali metal. The temperature at which the positive emission begins is (for the case shown in Fig. 10) closely the same as that for which the electron emission from the coating of alkali metal on the filament drops to negligible value. The positive emission, therefore, does not occur from the alkali metal on the filament, but is due to the alkali-metal particles which strike the cleaned-off tungsten filament. The magnitude of the positive current is independent of the filament

FIG. 10.



Thermionic currents obtained with a tube of the type shown in Fig. 9.

temperature in the temperature region below that at which electron emission from the filament itself occurs, but varies with the bulb temperature and therefore the pressure of the alkali-metal vapor.

THE MASSES OF THE POSITIVE CARRIERS.

The masses of the carriers may be deduced from the voltage-current relation as obtained in a tube with coaxial cylindrical electrodes such as that shown in Fig. 9. The formula to be used is as follows:[5]

$$i^{\frac{2}{3}} = k\left(\frac{e}{m}\right)^{\frac{1}{3}}\left(\frac{l}{r}\right)^{\frac{2}{3}} V$$

where

i = current;
l = length of collecting cylinder;
r = radius of collecting cylinder;

and

V = voltage.

When plotted on special paper in which the ordinates are proportional to the two-thirds power, the slope of the resulting straight lines is proportional to $\left(\frac{e}{m}\right)^{\frac{1}{3}}$. Assuming that the particles are singly charged, and using the ordinary value for e, the value of m can be obtained. In our case,

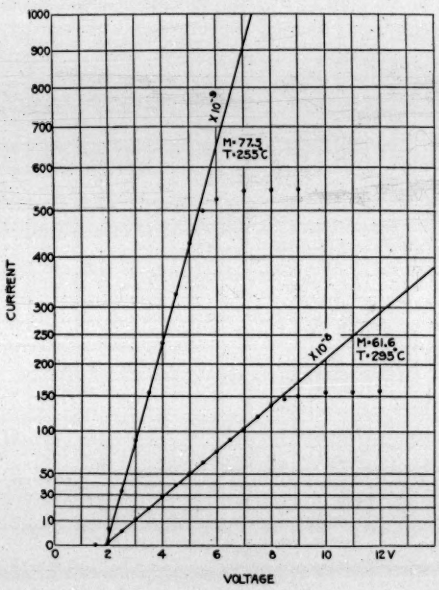
$$m = .493\,\frac{V^3}{i^2}$$

A typical set of data is shown in Fig. 11. Values for the masses obtained for the four alkali-metal vapors are shown in Fig. 12. The values of mass in each case *vary with the temperature of the alkali-metal vapor.* Variation of filament temperature within the range here considered has no effect on the apparent mass. It will be noted that the masses indicated for the low vapor temperatures, that is, temperatures in the neighborhood of room temperature, are at least several times the atomic mass. In the case of potassium, rubidium, and cæsium, the masses decline asymptotically with increase in temperature to the atomic value; indicating that with a sufficiently high temperature of the alkali-metal vapor, the positive carriers are metallic ions. In the case of sodium, the lowest value obtained is 46, which is equivalent to twice the atomic weight of sodium. While experimental difficulties prevented the attainment of higher temperatures in the case of sodium, there nevertheless appears to be no doubt that

the curve shown in Fig. 12 has very nearly reached its asymptotic value. Apparently then the lowest average mass attained by the sodium carriers is twice the mass of the sodium atom.

The observed variation of mass with temperature of the vapor was suspected to be some illusory effect, perhaps because of conditions which render the formula inapplicable. In order to

FIG. 11.

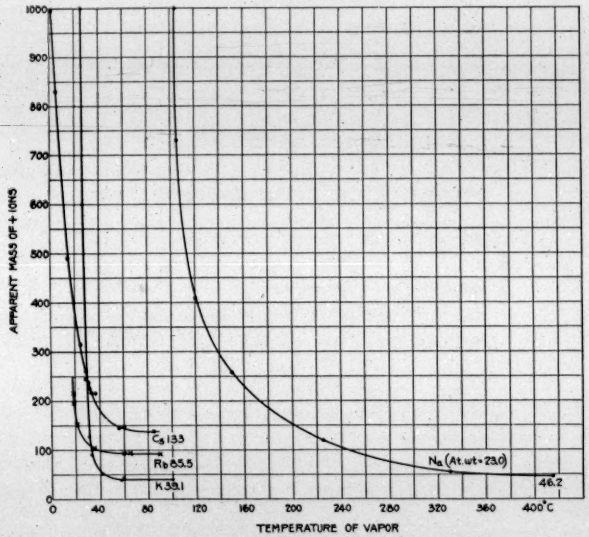


Typical data for the determination of $\frac{e}{m}$.

obtain a separate check on this point, attempts were made to determine the mass of the carriers by finding the effect of a magnetic field upon them. It is well known that by placing a cylindrical electrical system such as that here used along the lines of force of a magnetic field the carriers may be coiled into spiral paths, and, with a sufficiently intense field, actually prevented from reaching the exterior electrode. For this experiment a specially powerful

magnet was constructed capable of giving a field of 1600 gauss, and tubes of the type shown in Fig. 9 were used. The apparatus was first tested on the electron current, which was easily suppressed for low field values. It was then tried on the positive carriers in a sodium and in a potassium tube. The results are shown in Fig. 13. No attempt was made to determine exactly the field values for which the carriers should be completely blocked

FIG. 12.

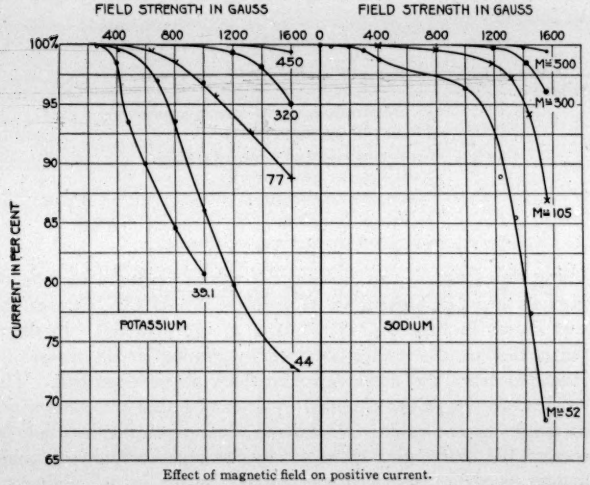


Masses of the positive carriers in the four alkali metals, as determined at various tube temperatures.

from the receiving electrode, as the magnetic field was only effective for values of potential drop between the electrodes too small to be accurately evaluated in view of the uncertainty as to the value of contact potential difference between the electrodes. The most intense fields available were, as the curves show, inadequate to suppress the positive current completely. What the curves do show, however, is that the amount of decrease in the current between the electrodes due to the magnetic field changes with the temperature of the vapor. For low vapor temperatures, the field

available was inadequate to affect the positive current appreciably. When, however, the vapor temperature was raised to a value at which the foregoing data indicate that the masses of the carriers are small, the magnetic field appreciably diminishes the strength of the positive current. These results with the magnetic field, therefore, confirm the results obtained from consideration of the voltage-current relation. Both lines of evidence indicate that at low temperatures there are present carriers of large mass. Neither experiment is, however, adequate to determine the exact

FIG. 13.



Effect of magnetic field on positive current.

masses. It is, of course, probable that there is present a mixture of single, double, triple, and other multiple atom groups. The existence of carriers of larger than atomic mass has previously been deduced from the banded absorption spectra exhibited by alkali-metal vapors even at temperatures considerably higher than those here used.

VAPOR PRESSURE.

If one assumes that each atom of alkali-metal vapor which strikes the hot filament is transformed into a positive ion, the magnitude of the positive current should give a measure of

the vapor pressure. For, knowing the area of the filament and the size of current, we can determine from kinetic theory the number of particles per cubic centimetre. This calculation is, however, only valid, apart from the initial assumption above mentioned, if the particles are of single atomic mass; which we have seen is probably not the case. The only reliable values of vapor pressure which can thus be obtained are those for which the vapor temperature is high enough to insure that the particles are of unit atomic mass.

The formula to be used in computing vapor pressure is as follows:

$$p = \frac{(2\pi\mu MkT)^{\frac{1}{2}}}{e} i$$

where

p = pressure in dynes per square centimetre;
u = mass of hydrogen atom;
M = atomic weight of ionized particles;
k = Boltzmann gas constant;
T = absolute temperature;
e = charge on electron;
i = current per unit area of filament.

Using this formula and plotting the values (reduced to mm. of Hg) in terms of logarithms of pressure *versus* $1/T$, data of the sort shown in Figs. 14, 15, 16, and 17 are obtained. In these, the circles are the values obtained by putting in the masses as indicated from the mass determinations above described. The crosses are the values obtained by assuming that the masses are of single atomic value. Neither of these sets of values can be correct, the latter being ruled out by the experimentally obtained masses as above described, the former by the inapplicability of the formula when other than unit atomic masses are concerned. The two sets of values, of course, converge toward higher temperatures. On the same sheets are plotted values for vapor pressures of the alkali metals as obtained by various investigators.[6] It will be noted that the values here obtained lie usually as close to values obtained by previous investigators as these latter do to each other.

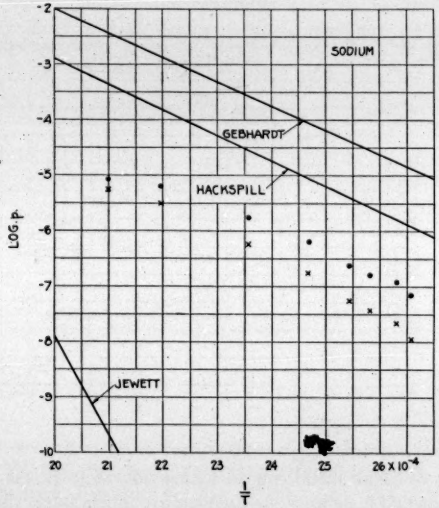
The results obtained upon calculating vapor pressures in this way appear to justify the assumption that, at least at the higher temperature studied, every alkali-metal atom striking the filament

produces a positive ion. At temperatures such that the positive ions are of single atomic mass, the procedure described appears to be a valid method for the determination of vapor pressures.

DISCUSSION.

The experiments above described establish the fact that it is possible to produce positive ions of the alkali metals, sodium, potassium, rubidium, and cæsium, by allowing the alkali-metal

FIG. 14.



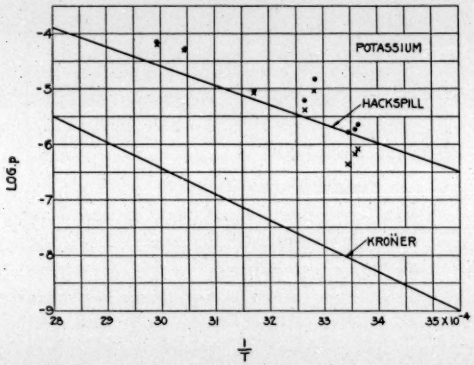
Vapor pressure *vs.* temperature values as deduced from positive-ray experiments. Sodium.

vapors to come in contact with a heated tungsten filament, and that the range of filament temperatures through which this phenomenon occurs is limited. The lower limit of temperature is set by the coating of the filament with a layer of alkali metal, and the upper limit (insofar as the production of positive ions *alone* is concerned) by the occurrence of the electron emission of the tungsten filament itself. It appears that at low temperatures of the alkali-metal vapor, the positive carriers are aggregates of metal atoms, positively charged, while at sufficiently high tem-

peratures the carriers are atoms of alkali metal which have been stripped of an electron. An exception, however, is presented by sodium, in which the carrier appears to consist of never fewer than two atoms.

For the explanation of the production of these positive carriers, it appears to be necessary to assume, first, the dissociation of the alkali-metal particles striking the filament, due to the high temperature to which they are raised, and, secondly, an attractive force exerted by the tungsten filament on electrons, but not on positive ions, in its near neighborhood. Thus, if we consider that when the tungsten filament reaches such a temperature that

FIG. 15.

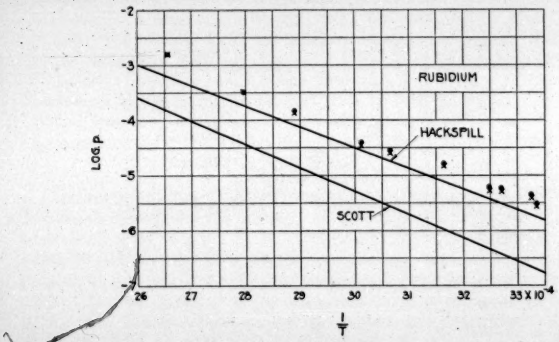


Vapor pressure *vs.* temperature values as deduced from positive-ray experiments. Potassium.

a coating of alkali metal can no longer adhere to it, the particles of alkali metal on striking the filament are immediately dissociated into positive ions and electrons, we have two cases to consider: One where the potential gradient is from a negative filament to a positive collector, and the other from a positive filament to a negative collector. With the filament positive it is apparent that the electrons will be immediately absorbed by the filament and the positive ions driven away. This case presents no particular problems. With the filament negative, however, it becomes necessary to explain why the electrons removed from the alkali-metal particles are not driven away and a current obtained in the reverse direction from that obtained in the first case.

A possible mechanism by which the phenomenon may be explained is as follows: If we assume that the work function of the tungsten surface results from a force which not only retards electrons issuing from the metal, but attracts electrons coming up from the outside, however produced, then if this attractive force is greater than the similar attractive force exerted by the alkali-metal particle on electrons, the electron which is produced by the temperature dissociation of the alkali-metal particle will be attracted more strongly by the tungsten, leaving the rest of the particle as a free positive ion. This amounts to assuming a strong positive field close to the filament which is practically unaffected by any externally applied field. If the ordinary

FIG. 16.

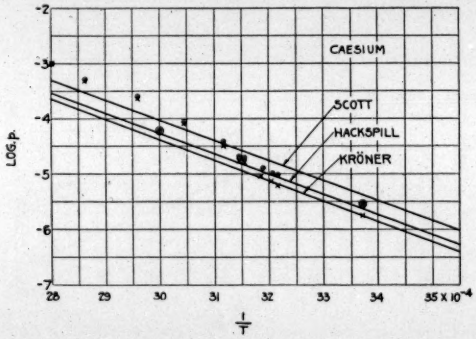


Vapor pressure *vs.* temperature values as deduced from positive-ray experiments. Rubidium.

electronic work function is due to this field, the experiments here described mean that we must assume a smaller work function for the positive ions. That such is actually the case is supported by recent work of Kunsman,[7] on the thermionic emission from iron filaments alloyed with alkali metal, which emit positive ions of alkali metal, under conditions which permit a measurement of their work function. On the view just presented it is easy to see that a tungsten surface of work function 4.52 volts will win out in the competition for the electron from a particle of any of the alkali metals, whose work functions are from 1.4 (Cs) to 3.2 (Na) volts. When, however, the particles decrease to atomic size, the work function as derived from experiments on

extended surfaces can no longer be considered as holding. In its place, it is probable that, for the limiting case, the ionizing potential (which is considerably higher) should be used. The ionizing potentials for the four alkali metals considered are, for sodium 5.1 volts, for potassium 4.3 volts, for rubidium 4.2 volts, for cæsium 3.9 volts. It will be noted that these are all, with the exception of sodium, smaller than the work function of tungsten. On this view, it should not be possible to obtain positive ions of single atomic mass from sodium. This, it will be recognized, is in accord with the experiment, in which ions of single atomic mass do not occur in sodium. If the general view here presented is correct, the work function of a particle composed of two sodium

FIG. 17.



Vapor pressure *vs.* temperature values as deduced from positive-ray experiments. Cæsium.

atoms has already dropped, in its progress from the ionizing potential value towards the value for massive sodium, sufficiently to bring it below 4.5 volts.

The explanation here offered is, essentially, that given by Langmuir and Kingdon,[8] who reported the discovery of these positive rays simultaneously with the present writer.[9] In a later communication, Langmuir and Kingdon[10] explain the relative proportions of positive and negative ions on the basis of the Saha equilibrium equation. In the opinion of the present writer, a complete theory must indicate some mechanism whereby, although positive and negative ions are produced in equal numbers (by the dissociating of neutral particles), one kind fails to appear. In

other words, it is still necessary, even if the Saha equation does agree with the facts, to explain how the equilibrium it predicts can come about under the conditions here obtaining.

The writer wishes to make acknowledgment to Mr. H. D. Arnold and Mr. C. Davisson for helpful discussions of the problems raised by these experiments, and to Mr. A. L. Johnsrud for assistance in the later stages of the experimental work.

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Gallium in Quartz Thermometer.—SYLVESTER BOYER, of the Thomson Research Laboratory of the General Electric Company (*Ind. and Eng. Chem.*, 1925, **17**, 1252–1253), has devised a thermometer which may be graduated to at least 1000° C. Electrolytic gallium is purified from its own oxide, and from hydrogen, zinc, and arsenic, and is sealed in a capillary tube of fused quartz of uniform bore. The thermometer is now calibrated and graduated. Gallium melts at 29.7° C., and boils at approximately 1700° C. The liquid metal may be undercooled to 1° or 2° C. before solidifying.

J. S. H.

Liquefied Hydrogen Sulphide as a Reagent.—CHARLES J. MOORE, of Hunter College (*Ind. and Eng. Chem.*, 1925, **17**, 1023), recommends the use of liquefied hydrogen sulphide, which is a by-product in the manufacture of diphenylthiourea from aniline and carbon disulphide, as a reagent in analysis. The liquid hydrogen sulphide is supplied in cylinders, from which it is released into a special gasometer with a liquid seal. The gaseous hydrogen sulphide is drawn from the gasometer as required in the operations of analytical chemistry. A constant supply of pure hydrogen sulphide is always available, and the cost of the gas is less than when produced in a generator from ferrous sulphide and hydrochloric acid.

J. S. H.

New Source of Arabinose.—ERNEST ANDERSON and LILA SANDS, of the University of Arizona (*Ind. and Eng. Chem.*, 1925, **17**, 1257–1258), recommend mesquite gum as a source of the pentose *l*-arabinose. Mesquite gum occurs as an exudate on the mesquite tree, *Prosopis juliflora*, and related botanical species which occur in Texas, Arizona, New Mexico, and northern Mexico. For the preparation of arabinose, mesquite gum is hydrolyzed by heating for three hours at a temperature of 80° C. in six times its weight of 4 per cent. sulphuric acid. The gum is dissolved in water; the requisite amount of sulphuric acid is then added; and the hydrolysis is carried to completion. Then barium hydroxide is added until the solution is neutral, and the sulphuric acid has been precipitated as its barium salt. After filtration, the solution is concentrated; the salts present are precipitated by addition of alcohol; and the alcoholic solution of the sugars is filtered, then concentrated and permitted to crystallize. The yield of crystalline arabinose is from 27 to 36 per cent. of the weight of gum taken; its melting-point lies between 140° and 155° C. It may be recrystallized from water, a mixture of water and alcohol, and glacial acetic acid. J. S. H.

Deflection of 40-inch Brick Wall under Pressure of One Finger Can Be Measured by Device Recently Constructed. (Bureau of Standards.)—The amount of deflection of a brick wall 40 inches thick, under the pressure of one finger, can be measured by an instrument recently constructed by C. G. Peters, of the Bureau of Standards, Department of Commerce. If one looks into the eyepiece while some one else walks across the floor, the deflection is apparently so great that one would suppose the whole building to be swaying back and forth as though made of cardboard.

The instrument makes use of the interference of light waves, and is very simple in construction. A glass plate is fastened to the wall of the building. Another plate is mounted close to this first plate in the tube of the instrument. Part of the light from a helium tube passes through the plate in the instrument and is reflected back by the plate on the wall into the eyepiece. The remainder is reflected directly from the plate in the instrument. The interference of these two sets of light rays causes light and dark bands to appear in the field of the eyepiece. When the distance between the two plates is changed the bands move across the field. Motion equal to the distance between two dark bands represents a deflection of about one one-hundred-thousandth of an inch.

ON THE RESTRAINT OF EXAGGERATED GRAIN GROWTH IN CRITICALLY STRAINED METAL.*

BY

G. L. KELLEY, Ph.D., and J. WINLOCK.

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Most metals, when subjected to cold work, undergo plastic deformation. The grains of metals which have been so strained show a tendency to grow. This tendency toward grain growth is nearly always augmented by an elevation in temperature. Such grain growth is usually attended by an equiaxing of grain structure and by certain other well-known physical changes. Some metals, for example, low carbon steel and aluminum, when subjected to a relatively small strain, undergo such internal changes that upon heating within a certain temperature range a rapid and large grain growth results. Metals so strained are described as critically strained, and the change of grain size is described as exaggerated grain growth.

The amount of cold work necessary to produce this particular degree of strain is often applied in manufacturing processes, such as in cold rolling and in stamping and drawing operations. The presence of critical strain frequently proves troublesome in that annealing subsequent to this cold work often may be carried on only at temperatures at which exaggerated grain growth does not occur, if an undesirable structure is to be avoided. Thus automobile-body sheet steel, after cold rolling, is frequently annealed in boxes to relieve the hardness produced by cold rolling without at the same time destroying the surface. The temperatures used are in the range at which many strained steels show exaggerated grain growth. It was with the object of learning whether this unfavorable condition might be avoided that this investigation was undertaken.

The phenomena of grain growth have been extensively described by many investigators. To attempt even a brief summary here would require too great space. We shall therefore concern ourselves principally with exaggerated grain growth in this paper. In 1912, Sauveur [1] noted that a low annealing temperature (650° C.) caused the development of a coarse crystalline

* Address delivered Friday, September 19, 1924, on the occasion of the celebration of the centenary of the founding of The Franklin Institute.

structure in low carbon steel which had been subjected to a certain amount of cold plastic deformation. Where the strain was more or less than this amount, heating to this temperature did not produce a coarse grain. This has been called Sauveur's "Critical Strain" hypothesis.

Stead [2] in 1898 and Joisten [3] in 1910 had made related observations. Since then, Sherry,[4] Robin,[5] Ruder,[6] Chappell,[7] Jeffries,[8] Howe,[9] and Mathewson and Phillips,[10] with many others, have added to the available knowledge on the subject. Jeffries has published an extensive list of very valuable papers on the general subject of grain growth. In the two papers mentioned in the references, he has collected statements of the laws governing grain growth in general and has included those dealing with exaggerated grain growth. Jeffries' statement of these laws follows:

(1) The grain size of cast metals is usually smaller the more rapid the rate of solidification.

(2) The grain size in cast metals which undergo no phase change in the solid state, cannot be changed appreciably by heating below the melting-point.

(3) Grain growth in the solid state may occur in—
- (*a*) worked metals;
- (*b*) compressed powders;
- (*c*) electrodeposited metals;
- (*d*) in iron which changes its allotropic form;
- (*e*) in alloys in which a new phase is formed in the solid state.

(4) The recrystallization temperature is lower—
- (*a*) the greater amount of deformation;
- (*b*) the smaller the grains prior to deformation;
- (*c*) the purer the metal;
- (*d*) the lower the temperature at which deformation is effected;
- (*e*) the longer the time of heating.

(5) In any given metal, the grain size after complete recrystallization is normally smaller, the lower the recrystallization temperature.

(6) Above the recrystallization temperature the grain size is normally greater, the higher the temperature and the longer the exposure.

(7) The higher the temperature, the more rapid the grain growth. At a temperature near the melting-point a few seconds is often sufficient to produce grains which may not change further on extended exposure.

(8) Certain conditions of non-uniformity sometimes give rise to the formation of abnormally large grains. This is called germination.

(9) The non-uniformities giving rise to germination are: Grain size contrast, strain gradients, temperature gradients, concentration gradients, and obstruction gradients.

(10) The presence of foreign matter or a second phase introduces mechanical obstruction to grain growth. The resistance to grain growth increases as the quantity of foreign matter or other phase increases and as this particle size decreases.

(11) The presence of a certain amount of obstruction matter promotes germination.

(12) The higher the germination temperature, the larger will be the grains and the quicker they will form.

(13) The more rapid the heating through the germinative temperature range, at least within limits, the finer will be the grain size.

With this helpful summary before us, we may proceed directly to a consideration of the immediate problem. Hillman and Coonan [11] have observed that low carbon steel which had been critically strained would not exhibit exaggerated grain growth if heated rapidly through the range in which this growth occurred. They used for this purpose, temperatures above 785° C. This method of avoiding exaggerated grain growth is not available for all metals, and it is especially not applicable in certain commercial processes of annealing, such as the box annealing of sheet steel. The present study deals with the effect of heating under various conditions at temperatures below those at which exaggerated grain growth occurs. It was thought that the inequalities in strain existing in different parts of the metal, and even in the same grain, might be turned to advantage in the partial destruction of strain gradients which lead to the larger grain growth in those instances when the degree and distribution of strain are most favorable. The piece of steel was regarded as being in a state of unstable equilibrium as to crystalline condition, and the factors of this

instability were considered to be the existing strain gradients, the contrast in grain size and in grain fragment size, and the condition of internal stress attending these. A piece of steel which has been subjected to slight plastic deformation regains most of its elasticity after a few days at room temperature, but using slightly elevated temperatures, such as 400° C., may bring about an equal recovery in one minute. It is well known that a piece of steel which has been subjected to a moderate amount of cold work may be slightly softened by heating to temperatures at which no change in micro-structure is visible. It is probable that both of these effects are produced mainly by action upon the amorphous material resulting from the distortion of the grains. In the latter case, however, it is conceivable that there is also a certain amount of crystal growth affecting the crystal fragments. This seems the most probable in that changes in hardness are not very noticeable until the lower edge of the temperature range is reached, in which crystal growth is known to occur. Jeffries points out that amorphous metal also probably plays an important part in recrystallization. Desch [12] states that strained, hardened metal is in an unstable condition and that its constituent molecules are under some degree of the restraint from which they are prevented from escaping by the high viscosity of the solid. Return to the stable condition takes place spontaneously although very slowly, and is enormously facilitated by the reduction of internal viscosity due to rise of temperature. Smithells [13] says that annealing metal which has been strained a small amount causes the disappearance of slip bands and twins, and no growth takes place. Many other statements could be quoted, all tending to show that the application of a moderate heat to critically strained metal might be expected to produce certain effects without making use of temperatures at which grain growth is noticeable.

While it is true that exaggerated grain growth is subject to the same laws as those which govern normal grain growth, it presents certain peculiarities. The case in which we are interested is that of a piece of metal which possesses a critical strain gradient and which upon annealing within a certain temperature range exhibits a rapidly formed, coarse grain growth. The degree of coarseness of grain produced under these circumstances is often greater than could otherwise be produced except by the use of extreme temperatures or very long periods of time.

The conditions existing in plastically deformed metals are probably very complex. Effects may be expected from such features as the distribution and degree of strain, the amount of fragmentation of crystals, the original grain size contrast, and the amount, character and distribution of non-metallic impurities. Critically strained metals will generally exhibit exaggerated grain growth when heated either slowly or rapidly to any point in the temperature range at which the conditions in the piece are productive of such growth. At the higher temperatures in the range, grain growth seems to be at a maximum both in speed and size. A study of the subject is made difficult by the irregularities in behavior which constantly appear. Of two apparently identical pieces of steel, one may first show grain growth at 500° C. and the other at 625° C. In another experiment, of two like pieces of metal exposed to the same annealing temperature, one may show general exaggerated grain growth while the other shows a fine equiaxed structure over most of the surface and exaggerated grain growth in only one relatively small area. The number and complexity of conditions related to the production of exaggerated grain growth interfere with satisfactorily laying down experiments which have general bearing and which may be well controlled. In the experiments a search was made for a set of conditions for heating which would alter conditions in the strained metal in such a manner that the factors operative in bringing about exaggerated grain growth would become so modified that this growth would be reduced in amount, or would occur only at higher temperatures and after the strain had been so far relieved that there would be a nearer return to the softness of the fully annealed state.

The experimental work was limited to low carbon steel and aluminum. Each sample of metal was cold rolled sufficiently to cause exaggerated grain growth when heated to a suitable temperature. The steel usually required a reduction of from 5 to 15 per cent. With these reductions, exaggerated grain growth was produced at various temperatures from 500° C. to 675° C. Exaggerated grain growth was most readily produced in the samples of aluminum when the reduction was between 15 and 25 per cent., and occurred at temperatures between 340° and 400° C. In one series of experiments the pieces were heated from 30 minutes to 96 hours at temperatures ranging from 15° to 60° C. below the lowest temperature at which grain growth had been

found to occur. The pieces were then heated to a temperature fairly high in the range in which grain growth had been previously produced. The suppression of grain growth or distinctly limiting it in pieces which had been given the preliminary heating, was taken to indicate success in inhibiting grain growth. On the other hand, the appearance of exaggerated grain growths in these was regarded as a failure to produce the expected result. In another series of experiments, pieces were heated for from four to eight hours at designated temperatures. The temperature was then raised by twenty-five degree increments and held for like lengths of time. The initial temperature was twenty-five degrees lower than that at which exaggerated grain growth occurred, and the final temperature was well within the range of growth. Control samples which had been heated to the lower and some of the higher temperatures, as well as some which had been heated only to the higher temperatures, were used for comparison. In this manner, it was possible to determine whether the heating at the lower temperatures merely raised the temperature at which exaggerated grain growth occurred, whether it prevented grain growth entirely, or whether it was without any effect at all.

Because of the many negative results obtained, a detailed account of our experiments is not given here. Instead there follows a brief general discussion and summary. Samples which had been previously heated to various lower temperatures, on being heated to the temperatures at which exaggerated grain growth might be expected to appear exhibited (1) no grain growth, (2) partial or local grain growth and (3) general exaggerated grain growth. Of course the first condition was the one usually met and the last was the least common. The encouragement which this might have afforded was in part offset by the failure of pieces to show exaggerated grain growth when heated to the proper temperature without preliminary heating at the lower temperature. The effect of heating aluminum at lower temperatures in no case prevented growth at some higher temperature, but there was a very noticeable tendency to raise the temperature at which grain growth occurred. Some samples of steel on heating at one of the lower temperatures developed a relatively fine equiaxed structure and could not be made to grow further at 750° C., as they would have done without preliminary heating. The most unsatisfactory samples of steel as concerns regularity of behavior were

those which had been annealed above Ac_3 before cold rolling. The case which seemed most frequently to result in the complete restraint of coarse growth was that in which the original sample of steel exhibited marked grain size contrast.

Contradictions and exceptions in the experimental work were frequent enough to interfere with a clear view of results. There have been, however, a number of positive results along with certain others which were only in part in harmony with the aim of these experiments. Such results as have been obtained make it possible to say that exaggerated grain growth in critically strained metals may often, although not always, be restrained or even prevented by a preliminary heating for a more or less lengthy period of time at temperatures below that at which this type of grain growth would normally occur.

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[13] "Effect of Impurities on Recrystallization and Grain Growth," *Jour. Inst. Metals*, 1922, Vol. 27, p. 131.

The Transmutation of Uranium into Uranium X. A. GASCHLER. (*Nature*, Sept. 12, 1925.)—The transmutation of the elements is in the air, just as was the case with telephony in the years preceding 1876. From Tokio and from Berlin has come the announcement of the transformation of mercury into gold. Now in *Nature* is made the claim that the author, also writing from Berlin, had anticipated Miethe in accomplishing this very striking transmutation, and that the discovery is described in a document deposited in the German Patent Office on May 3, 1922, where it is accessible to the curious. Even a more general claim is made for "the transmutation of mercury into other elements, when submitted to the effect of a strong electric discharge." After the document had been put in safe keeping, further experiments were made and important results attained. In a narrow vertical tube of fused quartz an electrode of tungsten was 15 cm. above a thin layer of uranium oxide resting on mercury in which was embedded the second tungsten electrode. The oxide was carefully freed from all radio-active constituents before it was used. After frequent electrical discharges of .3 or .4 ampere had passed for thirty hours from one electrode to the other, definite and growing radio-activity manifested itself by the presence of β-rays and γ-rays. Moreover, the radio-active material was separated by chemical means and its half-period when measured proved to be that of uranium X. "The β-ray and γ-ray activity of the uranium oxide freed from the mercury varied between 1.4 and 20 times the radio-activity of an equally large amount of uranium oxide in equilibrium with its decay products, and increased proportionally to the energy applied and to the time." When Nagaoka's method was applied and the oxide was mixed with vaseline, the resistance became so high that the discharge could leap only a short distance, but in compensation the energy was spent upon a small volume and after a half an hour considerable quantities of uranium X were detected.

The significance of these results lies, not in the accomplishment of a transmutation hitherto unknown, but in the acceleration of a transmutation long recognized as occurring spontaneously, but formerly believed to proceed upon the even tenor of its way quite unaffected by temperature, pressure or, indeed, by any controllable agents. G. F. S.

THE TRANSITION FROM GLOW TO ARC DISCHARGE AT ATMOSPHERIC PRESSURE.*

BY

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INTRODUCTION.

Two types of electric discharge are recognized, which at atmospheric pressure carry considerable current density at the cathode. These, the glow and arc, show markedly different cathode appearances and characteristics.

In the glow, the cathode current density is from 3 to 10 amperes per cm.^{2}, and the cathode drop is about 300 volts. This potential drop takes place across a dark space about .001 cm. thick, immediately adjacent to the cathode, and which separates it from the glow. The cathode may be cold, and need not contribute any metallic vapor to the glow, although it is also possible to have a glow from a molten cathode. In the arc discharge, the cathode-current density is 100 to 1000 times that of the glow, and the cathode drop is only 10 to 20 volts. The cathode spot from which the current issues is (usually) very hot, and a stream of metallic vapor issues therefrom. High temperature at the cathode seems to be essential for an arc. If, by proper cooling, a high temperature is prevented, discharge can only pass as a glow, with correspondingly high cathode drop.

Any theoretical explanation of the glow or arc seems necessarily to require the generation or liberation of free electrons at the cathode. The phenomena at the cathode suggest that the glow and arc differ as to the mechanism of the generation of these free electrons. In the glow, the cathode drop, 300 volts, across the cathode dark space, .001 cm. thick, is very nearly equal to the breakdown voltage between electrodes spaced .001 cm. apart. The ionization in the cathode dark space is therefore probably produced in the same way as that in the .001 cm. spark gap being broken down, and the electrons set free at the cathode are the result of collisions of positive ions with the cathode, or with molecules of gas very close to the cathode.

* Communicated by the Author.

In the arc, the cathode drop, about 15 volts, is too low for the generation of free electrons by collisions of positive ions. The very high temperature of the cathode spot suggests another alternative, namely, thermionic emission from the cathode. This is the generally accepted theory for the generation of the free electrons at the cathode of an arc.[1]

According to this theory then, a discharge will take the form of an arc if the cathode spot is at so high a temperature that the thermionic emission can supply a large part of the total current, that is, if the thermionic emission is of the order of amperes per cm.[2]. If, however, the cathode spot is too cool to give so copious an emission, then the discharge will take the form of a glow.

II. THERMIONIC THEORY OF GLOW TO ARC TRANSITION.

A discharge at atmospheric pressure of a few milliamperes will take the form of a stable glow with most electrode materials. If now the current is increased, at a certain limiting current, about 0.1 ampere, the glow suddenly changes to an arc. Stark[2] explained this by the thermionic theory of the cathode of an arc. When the current is first increased from its initial small value, the current density at the cathode, as is well known, remains approximately constant, but the area of the cathode spot increases. With increase of area of the cathode spot, the temperature of the cathode at the centre of the spot increases, and at the critical value of current reaches so high a value, that its thermionic emission suffices for an arc. Usually the complication of melting and volatilization of the electrode will occur before this point.

Another type of transition from glow to arc may be considered. A heavy current discharge may be suddenly started between cold electrodes, disruptively, by application of sufficient voltage. Then since the electrode material has a finite heat capacity and finite heat conductivity, a certain time must elapse before the electrode surface can become very hot. Hence, according to the thermionic theory, the discharge must start as a glow, and only after a certain time, which should be calculable from the thermal and thermionic constants of the electrode material, will it break into an arc.

[1] K. T. COMPTON: *Phys. Rev.*, 21, p. 266 (1923).
[2] STARK: *Ann. d. Physik.*, 12, p. 692 (1903).

III. INADEQUACY OF THE THERMIONIC THEORY.

The thermionic theory of glow-arc transition outlined above, while very satisfactory, as a qualitative explanation, seems to fail when put to quantitative test. Considering the first type of transition, let us calculate the relation between the current and the temperature of the cathode at the centre of the cathode spot. If W is the heat flow into the cathode per cm.^{2} and r is the radius of the spot, and k is the thermal conductivity of the material, then the temperature at the centre is given by

$$T = \frac{Wr}{k} \tag{1}$$

the electrode being considered as a semi-infinite solid.

The electrical input into the cathode dark space per cm.^{2} is Ei, where E is the cathode drop, and i is the current density. Nearly all of this energy goes into the cathode as heat.

If we substitute Ei for W in equation (1), we obtain

$$T = \frac{Eir}{k} \tag{2}$$

which errs in making T too large.

The total current I equals $\pi r^2 i$, so that (2) becomes

$$T = \frac{Ei^{1/2}}{k\pi^{1/2}}\sqrt{I} \tag{3}$$

Substituting numerical values, we get,

$$\left|\begin{array}{ll} \text{Copper,} & T = 90\ \sqrt{I},\ k = 1.0\ \times 4.18,\ E = 300,\ i = 5 \\ \text{Brass,} & T = 670\sqrt{I},\ k = 0.2\ \times 4.18,\ E = 350,\ i = 8 \\ \text{Iron,} & T = 530\sqrt{I},\ k = 0.17 \times 4.18,\ E = 300,\ i = 5 \\ \text{Platinum,} & T = 780\sqrt{I},\ k = 0.17 \times 4.18,\ E = 350,\ i = 8 \end{array}\right. \tag{4}$$

Equations (4) show that it would be necessary to go to many amperes in the glow in order to raise the temperature of a spot on the cathode the one to two thousand degrees necessary for thermionic emission. Nevertheless, the experimentally determined critical currents for glow-arc transition are always of the order of 0.1 ampere, and never greater than one ampere.

For the copper, brass, and iron, above, it may be argued that a layer of oxide forms, which so reduces the rate at which heat may be carried into the metal that high temperatures are reached even for 0.1 ampere, but this argument can hardly apply to the platinum. For this last metal Burstyn [3] definitely records a critical current of 0.08 ampere.

[3] BURSTYN: *Elektrotech. Zeit.*, June 30, 1920, p. 503.

Another explanation which might be advanced is that the current at the cathode in the glow at atmospheric pressure is not uniformly distributed over the cathode spot, so that some points may receive enough energy to raise them to a high temperature, even though the average energy density over the cathode is low. This might be due to some points of the metal surface having lower cathode drop than others, so that they take on an abnormal current density, which may be many times the normal.

Such points of abnormally low cathode drop are not observed in glow discharges at low pressures, but it may be argued that if the diameters of the abnormal spots are small compared with the thickness of the cathode dark space, they can hardly influence the current distribution there. At atmospheric pressure, however, where the cathode dark space shrinks down to 0.001 cm., these spots may begin to affect the current distribution considerably.

Let us test this explanation with platinum. Suppose an abnormal spot has a radius of one-tenth of the dark space, or about 0.0001 cm. If it were much smaller, it could not alter the current distribution in the dark space materially. Taking equation (2), if the temperature rise is to be 2000°, the current density in the spot would have to be, $i = \frac{2000 \times 0.17 \times 4.18}{350 \times .0001} = 40{,}600$ amperes/cm.^{2}. But this seems to be an absurdly high current density for a glow. If the abnormal spot diameter is equal to that of the dark space thickness, $r = .0005$, the current density for $T = 2000°$ by (2) is 8100 amperes/cm.^{2}, which is still absurdly high, and the total current in the spot is $\pi \times (.0005)^2 \times 8100$ or 0.158 ampere, which is larger than the total critical current for transition, 0.08 ampere observed by Burstyn.

The attempt to explain the second type of transition quantitatively by the thermionic theory is equally unsatisfactory. Here a large current glow, issuing from an initially cold cathode, changes into an arc when the cathode becomes sufficiently hot. Letting W be the heat flow into the cathode per cm.^{2}, k, c, and δ, the heat conductivity, heat capacity, and density, respectively, of the cathode material, t, the time in seconds, we have for the temperature rise of the cathode surface, treating it as the face of a semi-infinite solid entirely covered by glow,

$$T = \frac{W}{\sqrt{kc\delta\pi}} \sqrt{t} \qquad (5)$$

Probably not all of the electrical input into the cathode dark space goes into the cathode as heat, so if we substitute Ei for W, we obtain

$$T = \frac{Ei}{\sqrt{\pi kc\delta}}\sqrt{t} \tag{6}$$

which errs in making T too large.

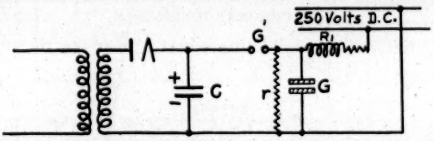
Substituting numerical values, we obtain

$$\left\{\begin{array}{llll} \text{Copper,} & T=226\sqrt{t}, & k=1.0\times 4.18, & c=.09\times 4.18, \ \delta=8.9, \ E=300, \ i=5 \\ \text{Brass,} & T=985\sqrt{t}, & k=0.20\times 4.18, & c=.088\times 4.18, \ \delta=8.4, \ E=350, \ i=8 \\ \text{Iron,} & T=509\sqrt{t}, & k=0.17\times 4.18, & c=.115\times 4.18, \ \delta=7.9, \ E=300, \ i=5 \\ \text{Platinum,} & T=1040\sqrt{t}, & k=0.17\times 4.18, & c=.036\times 4.18, \ \delta=21.4, \ E=350, \ i=8 \end{array}\right. \tag{7}$$

These equations show that the discharge should persist as a glow for a matter of seconds before the cathode reaches a high enough temperature for thermionic emission.

Experiments were carried out, however, which showed that the

FIG. 1.



transition from glow to arc is very much more rapid. Referring to Fig. 1, a condenser, 2 microfarads' capacity, was charged by means of a transformer and thermionic rectifier, until the gap G' would break down. This would occur at about 2500 volts. A discharge would then occur across the gap G made up of the metals to be tested. Impressed across G was also 250 volts from the direct current mains. The reactor R_1 served to keep the condenser discharge out of the direct current mains. The resistor r, 50,000 ohms, served to concentrate the condenser voltage, upon the gap G, during the charging period.

The condenser discharge through G could not have lasted for more than 10^{-5} seconds. If the discharge remained a glow during this time, then the 250 volts d.c. would not be able to maintain it, and the discharge would cease as soon as the condenser was discharged. If, however, the glow changed to an arc in this time, then the 250 volts would maintain it as a permanent arc.

Copper and brass electrodes were tried. In every case, as

soon as the condenser would discharge, a permanent arc was formed at G.

IV. THERMAL IONIZATION THEORY OF GLOW-ARC TRANSITION.

Because of the high thermal conductivity and capacity of metal cathodes, the thermionic theory fails to account quantitatively for the glow to arc transition. It is necessary to find some other mechanism of ionization or electron liberation which causes the glow to become unstable. The very high energy input into the cathode dark space, and the relatively low thermal conductivity and capacity of the gas, suggest that in spite of its close proximity to the cool cathode, some portions of this dark space reach temperatures high enough for thermal ionization, and that when this thermal ionization is sufficiently intense, the transition from glow to arc takes place.

V. TEMPERATURE NECESSARY FOR GLOW INSTABILITY DUE TO THERMAL IONIZATION.

Saha [4] derived the following equation for the thermal ionization of a gas:

$$\log \frac{x^2}{1-x^2} P = -\frac{5050\, V_i}{T} + 2.5 \log T - 6.69 \qquad (8)$$

where x is the fractional number of atoms ionized, P the pressure in atmospheres, V_i the ionizing potential in volts, and T, the absolute temperature. This formula shows that the per cent. ionization is a rapidly increasing function of the temperature until 100 per cent. ionization is approached. The curves of Fig. 2 show the progress of ionization with temperature for a metal, calcium, with a low ionizing potential, 6.1 volts, and for a diatomic gas H_2, with a high ionizing potential, 13.5 volts. For the former, ionization reaches 1 per cent. at about 4000° K., and for the latter at about 8000° K.

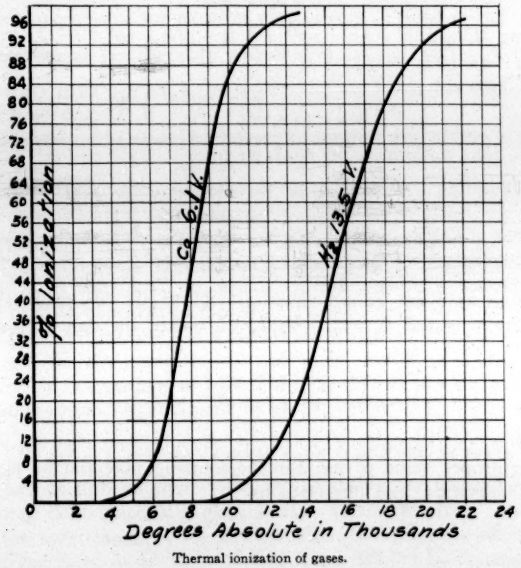
We may expect that the thermal ionization in the cathode dark space will begin to influence the current distribution and potential distribution in the dark space when the current density due to the thermal ionization is comparable with the normal current density, that is, when it is of the order of one ampere per cm.^{2}. To deter-

[4] SAHA: *Proc. Roy. Soc.*, **99**, p. 135 (1921).

mine the degree of ionization necessary for this current, we need to know the gradient, and the mobility of the electrons.

The gradient in the dark space varies from almost zero at the side more remote from the cathode, to something of the order

FIG. 2.



Thermal ionization of gases.

of 500,000 volts per cm. immediately next to the cathode. However, it is the side farthest from the cathode which will be the hottest. Let us consider then a hot layer of the cathode dark space in which the average gradient is 1000 volts per cm.

Following Compton,[5] the current density of positive ions will be

$$j = 3.27\,(10)^8 \frac{L\Omega N x e^2 E}{pT} \text{ amps./cm.}^2 \qquad (9)$$

where L is the mean free path in cm., Ω is the average molecular translational velocity, N is the number of molecules per cm.^{3}, x

[5] K. T. COMPTON: *Phys. Rev.*, 21, p. 288 (1923).

is the fraction of molecules ionized, e is the charge on an electron in e.s.u., E is the gradient in volts/cm., p is the gas pressure in dynes/cm.^{2} and T is the absolute temperature.

The current density of electrons is, according to Compton (*loc. cit.*, p. 278),

$$i = 242 \sqrt{M} j. \tag{10}$$

Taking $M = 30$, $N = 7.5 \times 10^{21}\ T^{-1}$, $\Omega = 2.60 \times 10^3\ T^{1/2}$, $L = 3.3 \times 10^{-8} T$, $p = 10^6$, $e = 4.77 \times 10^{-10}$, $E = 1000$, (10) substituted in (11) becomes

$$i = 5.5 \times 10^8 T^{-1/2} x \tag{11}$$

Hence for $i = 1$ ampere per cm.^{2}, we have

$$\begin{cases} \text{For } T = 2000^\circ & x = 8.15 \times 10^{-8} \\ \text{For } T = 3000^\circ & x = 1.0 \times 10^{-7} \\ \text{For } T = 4000^\circ & x = 1.15 \times 10^{-7} \\ \text{For } T = 5000^\circ & x = 1.22 \times 10^{-7} \end{cases} \tag{12}$$

If in applying Saha's equation (8) to air, we take as the ionizing potential $V_i = 16.0$ volts, we obtain the data (by slide rule)

$$\begin{cases} T = 4000^\circ & x = 1.1 \times 10^{-9} \\ T = 5000^\circ & x = 1.4 \times 10^{-7} \end{cases} \qquad V_i = 16.0 \tag{13}$$

However, Compton (*loc. cit.*, p. 287) believes that 8.6 volts is the proper value to use for the ionizing potential of air in Saha's equation, and this leads to

$$\begin{cases} T = 2000^\circ & x = 1.0 \times 10^{-10} \\ T = 3000^\circ & x = 7.1 \times 10^{-7} \end{cases} \qquad V_i = 8.6 \tag{14}$$

Comparing (12) and (13) we see that at a temperature of 5000° K. in the dark space, the current distribution should be considerably affected by the thermal ionization, and if (14) applies, this will happen at less than 3000° K.

There is another factor, however, which makes it seem likely that considerably lower temperatures will suffice for instability. Saha's equation (8) is derived on the basis of thermodynamic equilibrium. But an ionized gas in an electric field is not in a state of equilibrium. The electrons, under the influence of the field, acquire an energy of agitation, which may correspond to a considerable elevation in temperature. Thus, according to

Compton [6] the energy of agitation acquired by electrons, in final steady state under a gradient E is

$$U_i = \frac{lE}{2.13}\sqrt{\frac{M}{m}} \tag{15}$$

where l is the mean free path of the electron, M and m are the masses of molecule and electron, respectively. Taking $l = 7.4 \times 10^{-5}$ to correspond to the data above, and taking $\sqrt{\frac{M}{m}} = 233$, and $E = 1000$ volts per cm. (10) gives $U_i = 8.2$ volts, which corresponds to 65,000° K.

However, the layer of thermally ionized gas in the cathode dark space is so thin that the thermally generated electrons in it will not acquire their final steady state energy of agitation. But if it is equal in thickness to one-tenth of the total cathode dark space, that is, if it is about 10^{-4} cm., then Compton's formula (*Phys. Rev.*, **22**, p. 339, 1923) shows that under the gradient of only 1000 volts/cm., the electrons will acquire a temperature 770° higher than that of the gas.

The electrons being at a considerably higher temperature than the gas, Saha's equation will not apply, but it is evident that ionization due to thermal agitation will set in at much lower temperatures than are indicated by it.

VI. TEMPERATURE IN CATHODE DARK SPACE, STEADY STATE.

Let us now estimate what temperatures are reached in the cathode dark space of a glow at atmospheric pressure. Because of the narrowness of the cathode dark space, nearly all of the heat generated in it will be carried to the cathode by thermal conduction. As a first approximation let us suppose all of the heat is so conducted.

We need to know the thermal conductivity of gases at high temperatures. Because of lack of experimental data, we shall use the formulæ given by the kinetic theory of gases. Jeans' "Dynamical Theory of Gases" (page 306) gives for the heat conductivity

$$\theta = 1/3\nu\bar{c}l\,\frac{d\bar{E}}{dT} \tag{16}$$

where ν = number of molecules per cm.^{3}, $\bar{c}$ = average molecular

[6] K. T. COMPTON: *Phys. Rev.*, **22**, p 338 (1923).

velocity, l = mean free path, $\overline{E}$ = average molecular energy. Taking $\nu = 7.5 \times 10^{21} T^{-1}$, $\bar{c} = 2.60 \times 10^{3}\ T^{1/2}$, $l = 3.3 \times 10^{-8}\ T$, $\frac{d\overline{E}}{dT} = 4.12 \times 10^{-16}$, we get

$$\theta = 0.88 T^{1/2} \tag{17}$$

or in watts/cm.^{2}/°C./cm.,

$$\theta = 8.8 \times 10^{-6}\, T^{1/2} \tag{18}$$

This gives for 273° C., $\theta = .000146$, whereas the Smithsonian Tables, sixth edition, give $\theta = .0000568 \times 4.18 = .00024$.

The differential equation of heat flow in the dark space is

$$\frac{-d}{dx}\left(\theta \frac{dT}{dx}\right) = ei \tag{19}$$

where e is the electric gradient, and i is the current density.

If we take the gradient as varying linearly from zero at the outer edge of the cathode dark space, $x = L$, to $\frac{2V}{L}$ at the cathode, $x = 0$, where V is the cathode drop, and L the width of the cathode dark space, we have,

$$\frac{-d}{dx}\left(8.8 \times 10^{-6}\, T^{1/2} \frac{dT}{dx}\right) = 2\,\frac{Vi}{L^2}\,(L - x) \tag{20}$$

Solving with the boundary conditions, $T = To$, $x = 0$; $\frac{\partial T}{\partial x} = 0$, $x = L$,

$$T^{3/2} = T_0^{3/2} + 5.6 \times 10^{4}\,\frac{Vi}{L^2}\,(L^3 - [L - x]^3) \tag{21}$$

The maximum temperature will be given by

$$T_L^{3/2} = T_0^{3/2} + 5.6 \times 10^{4} WL \tag{22}$$

where W is the electrical input per cm.^{2} of cathode spot.

Using the data for platinum above, $W = 2800$, and taking $T_0 = 500°$ K. and $L = 10^{-3}$, we calculate

$$T_L \text{ (platinum)} = 3000° \text{ K.} \tag{23}$$

VII. ADEQUACY OF THERMAL IONIZATION THEORY FOR FIRST TYPE OF GLOW-ARC TRANSITION.

The temperature of 3000° K., calculated above for the cathode dark space for platinum, is undoubtedly sufficiently high for considerable thermal ionization; in fact, so high a temperature is probably not necessary. Starting with very small current in the glow, it seems likely that thermal ionization plays a part in

the cathode dark space long before the critical current for glow-arc transition is reached. The first effect of thermal ionization would be to reduce the gradient in the hot layer, thus reducing the effective thickness of the dark space and increasing the current density. For small currents, however, the increased energy input per cm.^{2} is compensated for in large part by the greater heat-conducting capacity of the thinner dark space, so that the further temperature rise is limited, and the glow remains stable with perhaps a slight reduction in the cathode drop.

The centre of the cathode spot, however, is hotter than the rest, and the dark space is thinner and the current density greater there. As the current is increased, the area of the cathode dark space increases, and the excess of temperature of the centre becomes larger. A point is reached (the critical current) where further increase of temperature and reduction of the cathode dark space thickness causes such an increase in current density that another considerable increase in temperature takes place in spite of the reduced cathode dark space thickness. This increase in temperature causes a still further considerable increase in current density, which again causes the temperature to increase, and so instability is obtained, the current all converging into the hottest spot.

Of course, the temperature of the cathode itself at the spot where the current is converging will rise to a high value, and it may become high enough for thermionic emission, in which case an arc according to the usual theory will result.

The basis of fact beneath these speculations is that the energy input into the cathode dark space is sufficient to raise its temperature by many thousand degrees. The thermal ionization theory of glow-arc transition is adequate to meet the test of quantitative calculation of the necessary temperature.

VIII. ADEQUACY OF THERMAL IONIZATION THEORY FOR SECOND TYPE OF GLOW-ARC TRANSITION.

In Section III an experiment was described, which showed that a disruptive discharge between initially cold electrodes changes into an arc or low-voltage discharge in less than 10^{-5} seconds. Let us examine whether the heat capacity of the cathode dark space is sufficiently small so that the thermal ionization theory is consistent with this fact.

Taking the specific heat of air as 0.24 and the density 0.0013, the thickness of cathode dark space as 0.001, and the energy input as 2800, we have for the rate of temperature rise, neglecting cooling,

$$\frac{dT}{dt} = \frac{2800}{4.18 \times 0.24 \times 0.0013 \times .001} = 2.1 \times 10^9 \text{ degrees per sec.} \qquad (24)$$

In 10^{-5} seconds this would give a temperature of 21,000 degrees. The thermal ionization theory is adequate, therefore, to account for the short time necessary for glow-arc transition.

IX. ARC WITH COLD CATHODE.

The transition from glow to arc, as has been shown above, takes place with the cathode too cold for thermionic emission. The heating of the cathode to a high temperature is a consequence and not the cause of the transition. During the transition, then, the discharge must take low voltage forms with the cathode still cold. That is, it must be an arc with cold cathode. The existence of such a discharge is contrary to generally accepted views.

We may go even further and assert that after the transition into the arc is completed, the cathode may still be too cold for thermionic emission. Refractory substances like platinum, carbon, tungsten, may perhaps reach temperatures high enough for thermionic emission, but for volatile metals, such as mercury, copper, etc., it is difficult to see how temperatures higher than their boiling-points can be reached.

The theory given above suggests that at an arc cathode with these metals, a layer of gas is strongly ionized thermally, and that this layer is so close to the cathode that the whole current can be carried to the cathode by positive ions only, with a moderate voltage. The author will elaborate on this theory of the arc in a later paper.

PHENOMENA DUE TO THE PASSAGE OF A BAR-MAGNET THROUGH A CIRCULAR COIL.*

BY

ENOS E. WITMER, Ph.D.

Harrison Research Fellow, University of Pennsylvania.

In a previous paper [1] the writer has discussed the currents in coupled circuits due to an e.m.f. of a particular type. This e.m.f. was produced by the passage of an ideal bar-magnet through a circular coil with uniform velocity, the trajectory of the magnet coinciding with the axis of the coil. Since this condition of coincidence is one which can only be realized approximately in practice, it is of interest to investigate the form of the e.m.f. curve for the more general case when the trajectory is any straight line which does not deviate too much from the axis of the coil. The first part of the present paper is a derivation of the e.m.f. formulas for this case. The second part of the paper is devoted to the experimental verification of the theory of the previous paper.

I. THE E.M.F. CURVES.

We consider below the e.m.f. induced in a circular coil by a magnet or magnetic pole moving with uniform velocity in a straight line, which is inclined to the axis of the coil by a small angle and which passes through the coil at a short distance from its centre. Three cases are treated in the order of their complexity. In the first case the moving element is a magnetic pole, in the second case a bar-magnet moving in the direction of its axis, and in the third case a magnet inclined to its trajectory. The formulas developed for the e.m.f. are in every case second order approximations in the quantities indicating the deviation of the trajectory from the condition of coincidence with the axis of the coil.

Notation:

E = e.m.f. induced in the circular coil by the passage of the bar-magnet;
E_1 = e.m.f. induced in the circular coil by the moving magnetic pole;
$2a$ = length of the bar-magnet;
b = radius of the circular coil;
V = velocity of the magnet;

* Communicated by Dr. C. B. Bazzoni.

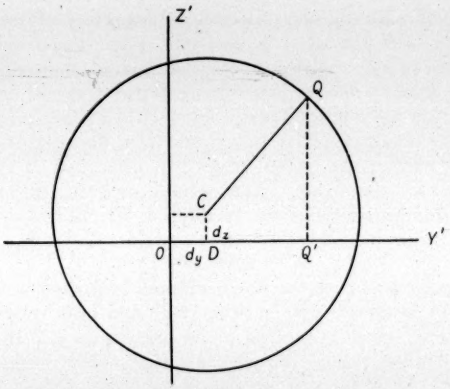
[1] Jour. Frank. Inst., 198, 217–229, 1924.

N = number of turns of wire in the circular coil;
m = pole strength of the magnet or the magnetic pole;
t = time. In the case of the moving magnetic pole time, t is measured from the instant the pole passes through the plane of the circular coil, and in the case of the bar-magnet, t is measured from the instant the centre of the magnet passes through the plane of the coil.

This notation corresponds with that used in the previous paper.

(1) *The E.M.F. Induced in a Circular Coil by a Moving Magnetic Pole.*—From the mathematical point of view this is the

FIG. 1.



fundamental case. The formulas for the other two cases are easily deduced from the formula for this case.

Fig. 1 is a diagram in the plane of the circular coil. C is the centre of the coil, and O the intersection of the trajectory of the magnetic pole with the plane of the coil. We take the point O as origin, the plane of the coil as the $y'z'$ plane, the projection of the trajectory of the magnetic pole on this plane as the Y'-axis, and the X'-axis perpendicular to the plane of the coil and making an acute angle θ with the positive direction of the trajectory. The positive direction of the Y'-axis is the projection of the positive direction of the trajectory of the magnetic pole. In Fig. 1 for the sake of definiteness assume X' directed toward the reader. The coördinates of C are $(0, d_y, d_z)$.

In all that follows terms of higher degree than the second in d_y, d_z, and $\sin\theta$ are neglected. Also $\sin\theta \doteq \tan\theta$.

The equations of the coil are

$$\left.\begin{aligned}(y'-d_y)^2+(z'-d_z)^2&=b^2\\ x'&=0\end{aligned}\right\}. \tag{1}$$

Now turn the X' and Y'-axes through the angle θ, thus making the trajectory the X-axis. The transformation equations are:

$$\left.\begin{aligned}x'&=x\cos\theta-y\sin\theta\\ y'&=x\sin\theta+y\cos\theta\\ z'&=z\end{aligned}\right\}. \tag{2}$$

Then change to cylindrical coördinates, using the transformation equations

$$\left.\begin{aligned}x&=x\\ y&=r\cos\varphi\\ z&=r\sin\varphi\end{aligned}\right\}. \tag{3}$$

Applying (2) and (3) to (1) and eliminating x from one of the resulting equations, we obtain

$$\left.\begin{aligned}x&=r\cos\varphi\tan\theta\\ r^2(1+\cos^2\varphi\tan^2\theta)-2r(d_y\cos\varphi\sec\theta+d_z\sin\varphi)&=b^2-d_y^2-d_z^2\end{aligned}\right\}. \tag{4}$$

Whence

$$r=r_0\equiv b\left\{1-\frac{1}{2}\cos^2\varphi\tan^2\theta-\frac{1}{2}\frac{(d_y\sin\varphi-d_z\cos\varphi)^2}{b^2}+\frac{d_y}{b}\cos\varphi\sec\theta+\frac{d_z}{b}\sin\varphi\right\}. \tag{5}$$

These are the equations of the coil in cylindrical coördinates. Hereafter any point on the coil will be designated by the coördinates (r_0, φ, x_0), and in general the subscript o shall indicate that the quantities to which it refers are evaluated at a point on the coil.

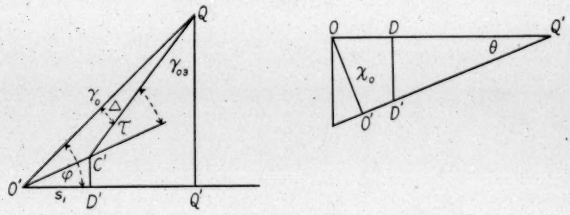
The e.m.f. induced in the circular coil is given by the formula

$$E_1=\frac{NV}{10^8}\int_0^{2\pi}H_r\,ds\,, \tag{6}$$

where ds is an element of arc of the coil and H_r is the component of the magnetic force at the element ds that is perpendicular to the trajectory of the magnetic pole and to the element ds. We shall find this component H_r by differentiation of the magnetic potential, a process which in this case requires considerable geometry and analysis. In order to carry out the integration in (6), the quantities H_r and ds must be expressed as functions of the angle φ.

$Q(r_0, \varphi, x_0)$ is the point on the coil at which we wish to find the effective component H_r of the magnetic force. In Fig. 2 (*a*), which is a diagram in the plane $x = x_0$, C' is the point of intersection of the axis of the coil and this plane, O' is the point $(0, 0, x_0)$ where the trajectory cuts the plane, the line $O'D'$ is parallel to the Y-axis, and $C'D'$ is perpendicular to $O'D'$. The effective

FIG. 2.



(*a*) (*b*)

component H_r acts along $C'Q$, which we shall designate r_{03}. Let $R(r_1, \varphi_1, x_0)$ be any point on $C'Q$ or $C'Q$ extended, and let $C'R = r_3$. The magnetic potential at R due to a magnetic pole at $(0, 0, x)$ is

$$P = \frac{m}{r_2}, \tag{7}$$

where

$$r_2^2 = (x - x_0)^2 + r_1^2 . \tag{8}$$

Hence the effective component of the magnetic force at Q is

$$H_r = -\left(\frac{\partial P}{\partial r_3}\right)_{r_3 = r_{03}} \equiv -\left(\frac{\partial P}{\partial r_3}\right)_0 . \tag{9}$$

Using (7) and (8)

$$H_r = \left(\frac{m r_1}{r_2^3}\frac{\partial r_1}{\partial r_3}\right)_0 .$$

Whence

$$H_r = \frac{m r_0}{r_{02}^3}\left(\frac{\partial r_1}{\partial r_3}\right)_0 , \tag{10}$$

where

$$r_{02}^2 = (x - x_0)^2 + r_0^2 . \tag{11}$$

We shall now derive some geometrical relations that will be needed in the subsequent work.

In Fig. 2 let

$$O'D' = s_1 ,$$
$$\angle\, C'O'D' = \psi ,$$
$$O'C' = s_2 ,$$
$$\angle\, QO'C' = \varphi_2 .$$

It is easily seen that

$$C'D' = CD = d_z . \tag{12}$$

Furthermore from Fig. 2 (*a*)

$$\varphi_2 = \varphi - \psi , \tag{13}$$
$$r_{02}^2 = r_0^2 + s_2^2 - 2s_2 r_0 \cos \varphi_2 , \tag{14}$$
$$r_1^2 = r_2^2 + s_2^2 + 2s_2 r_2 \cos \tau . \tag{15}$$

And from Fig. 2 (*b*)

$$s_1 = d_y \sec \theta - x_0 \tan \theta ,$$

whence, using equation (4),

$$s_1 = d_y \sec \theta - r_0 \cos \varphi \tan^2 \theta . \tag{16}$$

We shall now evaluate the partial derivative in equation (10). From (15)

$$r_0 \left(\frac{\partial r_1}{\partial r_2}\right)_0 = \left(r_1 \frac{\partial r_1}{\partial r_2}\right)_0 = r_{02} + s_2 \cos \tau . \tag{17}$$

From Fig. 2 (*a*)

$$\tau = \varphi_2 + \Delta ,$$
$$\cos \tau = \cos \varphi_2 - \sin \varphi_2 \cdot \Delta ,$$

and

$$\sin \Delta = \Delta = \frac{s_2}{r_{02}} \sin \varphi_2 .$$

Hence

$$\cos \tau = \cos \varphi_2 - \frac{s_2}{r_{02}} \sin^2 \varphi_2 . \tag{18}$$

From equation (14)

$$r_{02} = r_0 \left(1 + \frac{s_2^2}{r_0^2} - \frac{2s_2}{r_0} \cos \varphi_2\right)^{\frac{1}{2}}$$
$$= r_0 \left(1 + \frac{1}{2} \frac{s_2^2}{r_0^2} \sin^2 \varphi_2 - \frac{s_2}{r_0} \cos \varphi_2\right) . \tag{19}$$

Substituting (18) and (19) in (17),

$$r_0 \left(\frac{\partial r_1}{\partial r_2}\right)_0 = r_0 \left(1 + \frac{1}{2} \frac{s_2^2}{r_0^2} \sin^2 \varphi_2\right) - \frac{s_2^2}{r_{02}} \sin^2 \varphi_2$$
$$= r_0 \left(1 - \frac{1}{2} \frac{s_2^2}{r_0^2} \sin^2 \varphi_2\right) . \tag{20}$$

We must now express s_2 and $\sin \varphi_2$ in (20) as functions of φ. From (13)

$$\sin \varphi_2 = \sin \varphi \cos \psi - \cos \varphi \sin \psi \ , \tag{21}$$

and from Fig. 2 (*a*)

$$\sin \psi = \frac{d_z}{s_2} \ , \quad \cos \psi = \frac{s_1}{s_2} \ .$$

Hence

$$s_2 \sin \varphi_2 = s_1 \sin \varphi - d_z \cos \varphi \ .$$

Whence, using (16),

$$s_2 \sin \varphi_2 = d_y \sin \varphi - d_z \cos \varphi \ . \tag{22}$$

Substituting (5) and (22) in (20),

$$r_0 \left(\frac{\partial r_1}{\partial r_2} \right)_0 = b \left\{ 1 - \frac{1}{2} \cos^2 \varphi \tan^2 \theta - \frac{(d_y \sin \varphi - d_z \cos \varphi)^2}{b^2} + \frac{d_y}{b} \cos \varphi \sec \theta + \frac{d_z}{b} \sin \varphi \right\} . \tag{23}$$

The quantity on the right of the equality is a function of φ.

We shall now express r_{02}, which occurs in (10), as a function of the variable φ. From (4), (5), and (11)

$$\begin{aligned} r_{02}^2 &= x^2 + b^2 - 2bx \cos \varphi \tan \theta - 2xd_y \cos^2 \varphi \tan \theta - 2xd_z \sin \varphi \cos \varphi \tan \theta \\ &\quad + (d_y^2 - d_z^2)(\cos^2 \varphi - \sin^2 \varphi) + 4d_y d_z \sin \varphi \cos \varphi \\ &\quad + 2bd_y \cos \varphi \sec \theta + 2bd_z \sin \varphi \qquad (24) \\ &= X^2 + e \ , \end{aligned}$$

where

$$X^2 = x^2 + b^2 \ . \tag{25}$$

Substituting (24) in (10),

$$\begin{aligned} H_r &= \frac{mr_0}{X^3} \left(\frac{\partial r_1}{\partial r_2} \right)_0 \left(1 + \frac{e}{X^2} \right)^{-\frac{3}{2}} \\ &= \frac{mr_0}{X^3} \left(\frac{\partial r_1}{\partial r_2} \right)_0 \left(1 - \frac{3}{2} \frac{e}{X^2} + \frac{15}{8} \frac{e^2}{X^4} \right) . \end{aligned} \tag{26}$$

The element of arc ds of the coil is given by the formula

$$ds^2 = dx_0^2 + r_0^2 d\varphi^2 + dr_0^2 \ . \tag{27}$$

Using (4) and (5) in (27),

$$ds = b \left\{ 1 + \frac{1}{2} \sin^2 \varphi \tan^2 \theta - \frac{1}{2} \cos^2 \varphi \tan^2 \theta + \frac{d_y}{b} \cos \varphi \sec \theta + \frac{d_z}{b} \sin \varphi \right\} d\varphi \ . \tag{28}$$

Combining (6), (23), (26), and (28),

$$E_1 = \frac{p}{X^2} F(x) = pG(x, d_y, d_z, \theta) \ , \tag{29}$$

where

$$p = \frac{2\pi N b^2 V m}{10^8}, \tag{30}$$

$$F(x) = 1 - \frac{1}{4}\tan^2\theta + \frac{9}{2}\frac{x d_y \tan\theta}{X^2} - 3\frac{d^2}{X^2} + \frac{15}{4}\frac{b^2 d^2}{X^4} + \frac{15}{4}\frac{b^2 x^2 \tan^2\theta}{X^4} - \frac{15}{2}\frac{b^2 x d_y \tan\theta}{X^4}, \tag{31}$$

and

$$d^2 = d_y^2 + d_z^2. \tag{32}$$

Putting $x = Vt$ in (29),

$$E_1 = p\frac{F(Vt)}{(V^2t^2 + b^2)^{\frac{3}{2}}}. \tag{33}$$

Let

$$\left.\begin{aligned} c &= \frac{a}{b} \\ u &= \frac{Vt}{b} \\ g_y &= \frac{d_y}{b} \\ g_z &= \frac{d_z}{b} \\ g^2 &= g_y^2 + g_z^2 \end{aligned}\right\}. \tag{34}$$

Using these equations, equation (33) can be put into the form

$$E_1 = \frac{p}{b^3}\frac{1}{U^3}\zeta(u), \tag{35}$$

where

$$U = \sqrt{u^2 + 1}, \tag{36}$$

and

$$\zeta(u) = 1 - \frac{1}{4}\tan^2\theta + \frac{9}{2}\frac{u g_y \tan\theta}{U^2} - 3\frac{g^2}{U^2} + \frac{15}{4}\frac{g^2}{U^4} + \frac{15}{4}\frac{u^2\tan^2\theta}{U^4} - \frac{15}{2}\frac{u g_y \tan\theta}{U^4}. \tag{37}$$

These formulas give the e.m.f. in volts when the quantities on the right of the equality are expressed in c.g.s. units.

(2) *The E.M.F. Induced in a Circular Coil by a Bar-magnet Moving in the Direction of Its Axis.*—The trajectory of the magnet is assumed to be the same as the trajectory of the magnetic pole in the previous case. At the time t the two poles are at the points $(0, 0, Vt \pm a)$, or what is the same $x = Vt \pm a$. Hence, remembering that the poles have unlike signs, we have from equations (25) and (29)

$$E = p\left\{\frac{F(Vt+a)}{\left[(Vt+a)^2+b^2\right]^{\frac{3}{2}}} - \frac{F(Vt-a)}{\left[(Vt-a)^2+b^2\right]^{\frac{3}{2}}}\right\}. \tag{38}$$

Using equation (34), this can be put into the form

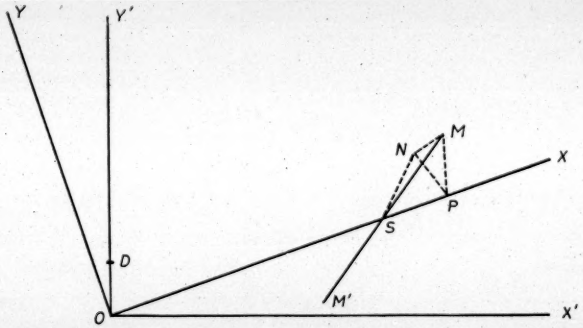
$$E = \frac{p}{b^2}\left\{\frac{1}{U_1^3}\zeta(u+c) - \frac{1}{U_2^3}\zeta(u-c)\right\}, \tag{39}$$

where

$$\left.\begin{aligned} U_1 &= \sqrt{(u+c)^2+1} \\ U^2 &= \sqrt{(u-c)^2+1} \end{aligned}\right\}. \tag{40}$$

(3) *The E.M.F. Induced in a Circular Coil by a Bar-magnet Inclined to Its Trajectory.*—The trajectory of the centre of the magnet is assumed to be the same as the trajectory of the magnetic pole in Case 1. In that case the quantities x, d_y, d_z, which occur in equations (29) and (31), were determined in a very definite manner by the position of the magnetic pole, its trajectory, and the plane of the coil. In this case the quantities

FIG. 3.



$$x,\ d_y,\ d_z;\quad x_1,\ d_{y1},\ d_{z1};\quad x_2,\ d_{y2},\ d_{z2}$$

are determined in the same manner by the positions and trajectories of the centre of the magnet, its leading pole, and its lagging pole, respectively.

In Fig. 3, where the notation corresponds with that used in Figs. 1 and 2, X is the trajectory of the centre of the magnet MM', O is the point where the X-axis intersects the plane of the coil, OY' is in the plane of the coil, OX' is perpendicular to the

plane of the coil, and $\angle XOX' = \theta$. To define the position of the magnet with respect to its trajectory, we use the angles θ' and φ'. Let $\angle MSP = \theta'$, while φ' we define as the angle MPN between the plane MPS and the XY plane measured counter-clockwise, *i.e.*, from the positive Y-axis toward the (positive) Z-axis.

Putting $x = Vt$, it can be shown from the geometry indicated in Figs. 1 and 3 that

$$\left.\begin{aligned} x_1 &= Vt + a\cos\theta' - a\sin\theta'\cos\varphi'\tan\theta \\ d_{y1} &= d_y - a\sin\theta'\cos\varphi'\sec\theta \\ d_{z1} &= d_z - a\sin\theta'\sin\varphi' \\ x_2 &= Vt - a\cos\theta' + a\sin\theta'\cos\varphi'\tan\theta \\ d_{y2} &= d_y + a\sin\theta'\cos\varphi'\sec\theta \\ d_{z2} &= d_z + a\sin\theta'\sin\varphi' \end{aligned}\right\} \qquad (41)$$

Using (29), the e.m.f. in this case is

$$E = p\left\{ G(x_1, d_{y1}, d_{z1}, \theta) - G(x_2, d_{y2}, d_{z2}, \theta) \right\} . \qquad (42)$$

Since this formula is a second order approximation in d_{y1}, d_{z1}, d_{y2}, d_{z2}, and θ, it will in general be valid only for values of θ', which do not make the corresponding values of the first four of these quantities too large.

Special Cases.—There are certain special cases in which the formulas for Cases 2 and 3 simplify considerably.

(*a*) If in Case 2, $\theta = 0$, so that the trajectory of the magnet is perpendicular to the plane of the coil and intersects that plane at a distance d from the centre of the coil, equation (39) reduces to

$$E = \frac{p}{b^3}\left\{ \frac{1}{U_1^3}\left[1 + \left(\frac{15}{4}\frac{1}{U_1^2} - 3 \right)\frac{g^2}{U_1^2} \right] - \frac{1}{U_2^3}\left[1 + \left(\frac{15}{4}\frac{1}{U_2^2} - 3 \right)\frac{g^2}{U_2^2} \right] \right\} . \qquad (43)$$

(*b*) If in Case 2, $d_y = d_z = 0$, so that the magnet passes through the centre of the coil along a trajectory, making an angle θ with the axis of the coil, equation (39) reduces to

$$E = \frac{p}{b^3}\left\{ \frac{1}{U_1^3}\left[1 - \frac{1}{4}\tan^2\theta + \frac{15}{4}\frac{(u+c)^2\tan^2\theta}{U_1^4} \right] - \frac{1}{U_2^3}\left[1 - \frac{1}{4}\tan^2\theta + \frac{15}{4}\frac{(u-c)^2\tan^2\theta}{U_2^4} \right] \right\} . \qquad (44)$$

Independent methods of deriving (43) and (44) show that they are third order approximations, since the third order approximations contain no terms of the third degree in the deviating quantities, d_y, d_z, and θ.

(*c*) Finally in Case 3, if we put $\theta = d_y = d_z = 0$, equation (42) becomes

$$E = p\left\{\frac{1}{T_1^3}\left[1+\left(\frac{15}{4}\frac{b^2}{T_1^2}-3\right)\frac{a^2\sin^2\theta'}{T_1^2}\right] - \frac{1}{T_2^3}\left[1+\left(\frac{15}{4}\frac{b^2}{T_2^2}-3\right)\frac{a^2\sin^2\theta'}{T_2^2}\right]\right\}, \quad (45)$$

where

$$T_1 = \sqrt{(Vt + a\cos\theta')^2 + b^2}$$

$$T_2 = \sqrt{(Vt - a\cos\theta')^2 + b^2}.$$

In this case the trajectory of the centre of the magnet passes perpendicularly through the centre of the coil, and the magnet is inclined to its trajectory by an angle θ'.

(*d*) The simplest case is, of course, the one when all the deviating quantities d_y, d_z, θ, and θ' are zero. In this case $\zeta(u) = 1$ and equations (39) and (42) reduce to

$$E = \frac{p}{b^3}\left\{\frac{1}{U_1^3} - \frac{1}{U_2^3}\right\} = \frac{p}{b^3}\Phi(u). \quad (46)$$

This is the form of the e.m.f. curve used in the previous article.

The Maxima and Minima of the E.M.F. Curve When the Trajectory of the Magnet Is the Axis of the Coil.—The curve we shall consider is the one for the simplest case, given by equation (46). This (u, E) curve has one maximum and one minimum situated at equal distances from the origin. The values of u at which these numerical maxima occur are given by the real roots of the equation

$$\frac{\partial}{\partial u}\Phi(u) = 0. \quad (47)$$

This equation when rationalized is of the fifth degree in u^2 and its coefficients are polynomials in c^2, so that it is impossible to solve for the roots as functions of c. It has been found, however, that these roots, which we shall designate $u_m(c)$, can be represented to a high degree of precision by the empirical formula

$$u_m(c) = \pm\sqrt[j]{c^j + \left(\frac{1}{2}\right)^j}, \quad (48)$$

$$j = 2.1092 + \frac{1.206\,c}{1 + .1467\,c}.$$

And to within 3.5 per cent. by the empirical formula

$$u_m(c) = \pm\sqrt[3]{c^3 + \left(\frac{1}{2}\right)^3}. \quad (49)$$

Table I shows the degree of accuracy of these two empirical formulas.

TABLE I.

$\frac{1}{c}$	$= u_m(c)/c$		
	From Eq. (47).	From Formula (48).	From Formula (49).
0	1.0000	1.0000	1.000
1	1.0341	1.0341	1.040
2	1.2963	1.2963	1.260
4	2.1498	2.1499	2.080
6	3.1039	3.1011	3.037
∞	$\frac{1}{2}\frac{1}{c}$	$\frac{1}{2}\frac{1}{c}$	$\frac{1}{2}\frac{1}{c}$

The numerical maxima given by $u = u_m(c)$ have an interpretation with reference to the magnet alone independently of the coil. Since this interpretation follows easily from the manner in which the e.m.f. curve is dependent on the magnetic field, we shall omit the proof and merely state the interpretation.

Taking the axis of the magnet as the l-axis, and the centre of the magnet as origin, let (b, φ, l) be the cylindrical coördinates of any point P. Let H_b be the component of the field due to the magnet at the point P in the direction of the line through P whose equations are $\varphi = \text{const.}$, $l = \text{const.}$ Now as b remains constant, and l varies, H_b varies and is numerically a maximum at two values of l given by

$$l = l_m = bu_m(c) = a\frac{u_m(c)}{c},$$

where

$$c = \frac{a}{b}.$$

As b varies the points (b, φ, l_m) generate a two-sheeted surface of revolution coaxial with the magnet. The shape of this surface is shown in Fig. 4, which is a section by a plane through the axis of the magnet BE. The sections of the surface are ABC and DEF, which are the curves (l_m, b) or $(au_m(c)/c, a/c)$. These curves were plotted from Table I. The latter expression for the coördinates of points on the curve shows that the length of the magnet does not affect the shape of this surface of revolution but only its magnitude. Since

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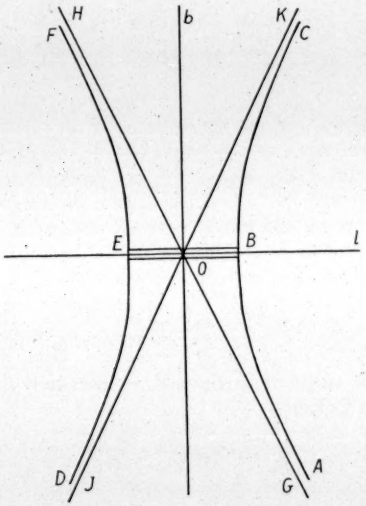
$$\lim_{b \to \infty} \frac{l_m}{b} = \lim_{c \to 0} \frac{a u_m(c)}{c} \Big/ \frac{a}{c} = \lim_{c \to 0} u_m(c) = \pm \frac{1}{2},$$

the cones $l = \pm \frac{1}{2} b$, whose traces are JOK and GOH in the figure, are asymptotic to this surface.

Remarks.—An examination of the preceding formulas for E, in particular equations (31) and (37), shows that all the terms

FIG. 4.



in the deviating quantities d_y, d_z, θ, and θ', are of the second degree in those quantities. If we take into consideration the fact that U_1, U_2, and U are always greater than unity, and that the e.m.f. is practically zero except for numerically small values of u, it can easily be shown that even relatively large values of the deviating quantities g_y, g_z, and θ give a value of $\zeta(u)$ in equation (37) only slightly different from unity. It follows, therefore, that even relatively large deviations from the conditions assumed for equation (46) produce only a small change in the resulting e.m.f.

II. EXPERIMENTAL VERIFICATION OF THE THEORY OF THE PREVIOUS PAPER.

The problem investigated in the previous paper [1] may be stated as follows: Two electrical circuits containing only resistance and inductance are magnetically coupled by an air core transformer. In the primary is a circular coil. An ideal bar-magnet, whose axis coincides with the axis of the coil, moves along this axis with a uniform velocity, thus generating a momentary electromotive force. The problem is to derive expressions for the currents in the primary and secondary as functions of the time. The experimental tests described in brief below were made to verify the formulas thus derived, namely (15) and (16), of the previous paper.

The experiments were made with a General Electric oscillograph. The circular coil was supported in a horizontal plane outside a first-floor window. The magnet was suspended directly above the centre of the coil from a platform outside the second-story window above by means of a piece of fuse wire, which could be blown by pressing a key at the oscillograph. A pasteboard tail kept the magnet vertical during its fall. Since, as has just been shown, deviations from the ideal conditions assumed in deriving equation (46) produce only second order effects on the e.m.f. curve, no special precautions were taken to ensure the magnet passing through the centre of the coil. One vibrator of the oscillograph was in the primary, another in the secondary, while the third carried 60-cycle a.c. for timing. When everything was ready the magnet was released by pressing the key which blew the fuse, and the trigger of the oscillograph pulled when the magnet appeared in the window.

Since the velocity of the magnet is assumed uniform in the theory, a calculation of the change of velocity in passing through the coil is of some importance. In our case the height of fall was 342.5 cm., $g = 980.2$ cm./sec.^{2}, whence by the formula

$$V = \sqrt{2gh}$$

$$V = 819 \text{ cm./sec.}$$

The important part of the e.m.f. curve was in our case the part generated by the magnet as it moved from $x = -2a$ to $x = 2a$, a distance of $4a$ or 50 cm. A calculation of the change of velocity in this distance gives $dV = 60$ cm./sec., which is 7.3 per cent.

In the oscillograms, Figs. 5 and 6, the upper curve is the secondary current with its zero line, the middle curve is 60-cycle

FIG. 5.

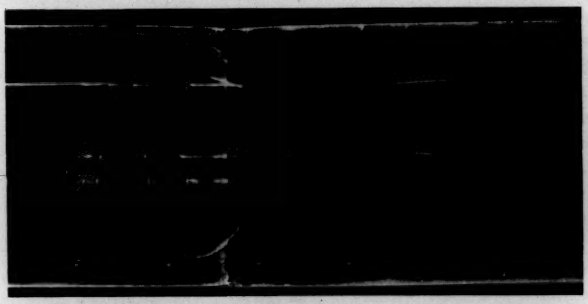
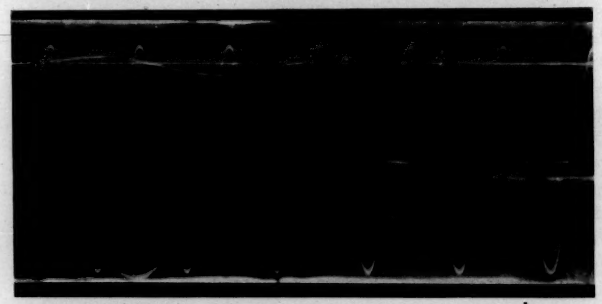


FIG. 6.



a.c. with its zero line, and the lower curve is the primary current with its zero line.

For the notation used below, the reader is referred to the previous paper.

The constants for the experimental arrangement used to obtain Fig. 5 are

$2a = 25.0$ cm.	$R_2 = 3.77$ ohms
$b = 10.65$ cm.	$L_1 = 95.9$ mil henries
$V = 819$ cm./sec.	$L_2 = 58.5$ mil henries
$R_1 = 7.95$ ohms	$M = 61.0$ mil henries

Whence

$c = 1.174$ $\alpha_2 = .984$
$k = .815$ $\alpha = 6.08$
$\alpha_1 = 1.265$ $\beta = .609$

For the oscillogram, Fig. 6, a, b, V, and c have the same values as in the preceding case, and

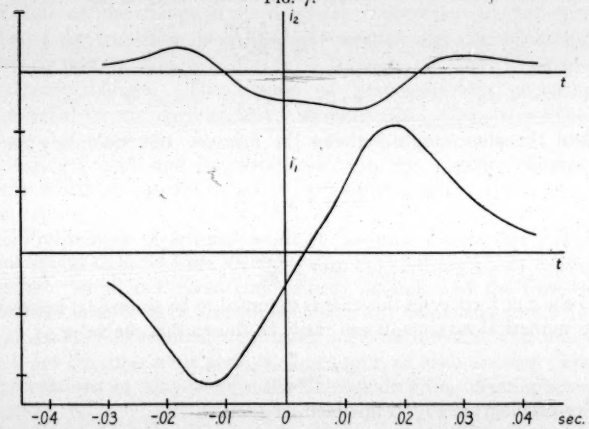
$R_1 = 7.43$ ohms $L_1 = 28.3$ mil henries $M = 13.0$ mil henries
$R_2 = 3.79$ ohms $L_2 = 16.0$ mil henries

Whence

$k = .611$ $\alpha_2 = 3.61$ $\beta = 2.36$
$\alpha_1 = 4.01$ $\alpha = 9.82$

Mere inspection of these oscillograms reveals differences which are in accord with the conclusions stated in the section of

FIG. 7.



my previous paper entitled, "Approximations and Interpretation of Results." In Fig. 5 the secondary curve crosses the time-axis twice, but the second crossing is not very pronounced. In the case of Fig. 6, where α and β are larger, the second crossing of the secondary curve is quite distinct, and it is evident that we are approaching the limiting case (c) of the previous paper, where the secondary curve is the derivative of the primary curve.

The computed curves corresponding to oscillogram Fig. 6 are shown in Fig. 7. Considering the divergence of the experimental conditions from the ideal conditions assumed in the theory, the agreement is good. The time scale on the computed curve

is larger than the time scale on the oscillogram. This may be due to the fact that in making the computations we assumed the poles to be at the ends of the magnet. Actually the poles are fictitious, and if assumed to exist should be at some distance from the ends of the magnet.

It is interesting to note that in the case of oscillogram Fig. 6, the time lags can be computed with a fair degree of accuracy from the formulas for the phase relations for the steady state in coupled circuits by assuming the e.m.f. given by equation (46) to be sinusoidal between its numerical maxima. As is well known, if the impressed e.m.f. in the primary is $E = E_0 \sin \omega t$, the angle of lag of the primary current behind the e.m.f. is given by

$$\tan \varphi = \frac{(L_1 - L_2 P_0^2)}{R_1 + R_2 P_0^2} ,$$

where

$$P_0^2 = \frac{M^2\omega^2}{R_2^2 + L_2^2\omega^2} .$$

And the phase angle between the primary and secondary currents is

$$\frac{\pi}{2} + \theta \text{ or } \theta - \frac{\pi}{2}$$

where

$$\tan \theta = \frac{L_2\omega}{R_2} .$$

If the e.m.f. curve in this case is assumed to be sinusoidal between its numerical maxima, it can easily be shown that the value of

$$\omega = \frac{V}{2bu_m(c)}\pi .$$

For oscillogram Fig. 6 this method gives

$$t_{01} = .00328 \text{ sec.}$$
$$t_{02} = -.00822 \text{ and } .0228 \text{ sec.}$$

By exact computation from Fig. 7

$$t_{01} = .00365 \text{ sec.}$$
$$t_{02} = -.00960 \text{ and } .0224 \text{ sec.}$$

An attempt to compute the phase relations of the primary and secondary currents in Fig. 5 by this short-cut showed that for the smaller values of α and β this method is of no value.

In conclusion the writer wishes to acknowledge his indebtedness to Dr. C. B. Bazzoni for valuable suggestions regarding the experimental work.

DIRECTION AND INTENSITY CHANGES OF RADIO WAVES.*

BY

CHARLES C. BIDWELL, Ph.D.

IN CONNECTION with the country-wide radio fading tests carried on during the present year by the U. S. Bureau of Standards, observations on direction changes as well as intensity changes were undertaken at Cornell University with the purpose of studying the change in the character of reception which occurs during the transition from daylight to dark and also of noting any correlation which might exist between the directional and intensity changes. The Bureau of Standards was primarily interested in the correlation of intensity data taken simultaneously by observers situated at widely different points. The directional work and its correlation with the intensity observations at Ithaca appear, therefore, as proper material for a separate report.

Preliminary directional work at the time of the April tests was found to be of little value because not continued over a long enough period nor taken continuously enough. At the time of the May tests, a more determined effort was made, and successful continuous observations were taken on both intensity and direction for the three-hour periods, six to nine, of each evening. The observations in May were made on signals from Westinghouse station, KDKA, and in August, on signals from the General Electric station, WGY. For the purpose of the tests these stations sent out on their regular carrier wave a sustained audio-frequency note beginning at 5:30 o'clock and continuing until time for the regular program material. The intensity measurements were made at Rockefeller Hall (the physics building) by Messrs. C. W. Gartlein and E. E. Zimmerman, using a five-tube neutrodyne set and recording on a chronograph the deflections of a galvanometer placed in the plate circuit of the last tube. The recording was not automatic but was effected by following the movements of the needle with a pen. Correction was made for any change in amplification during a run, but in most series

* Communicated by the Author.

of observations no circuit changes were made. Directional observations were made, using a three-foot loop of ten turns and a four-tube regenerative set composed of one stage of radio-frequency amplification, detector and two stages of audio-frequency amplication. In making directional settings the loop was always set for a minimum, this being far sharper than the setting for maximum. When the regular program material came on, it was found much easier to make settings on a sustained note, obtained by heterodyning with the carrier wave rather than to make settings directly on the voice or music. The pauses and the intensity changes associated with the regular program material were confusing but, when the station was slightly tuned off and a beat-note brought in, very certain and satisfactory settings were possible. When not changing too rapidly the settings were certain within about one degree.

The directional observations by the author were made in a barn in the country about one and one-half miles southeast of Rockefeller Hall and were free from interference of other sets or of power lines. On two occasions, May 25th and August 14th, directional measurements were also obtained by Mr. H. J. Reich, who on the former date took up a station about one mile south of the author and on the latter, about four miles west, across Cayuga Lake.

On the original chronograph intensity records one inch represented two minutes and the fluctuations throughout that interval were given, but in the condensed plots here shown, the average values of the deflections over one-minute intervals are shown. Directional settings were usually made about four to the minute and these averaged for each half minute. The settings plotted are the readings of a pointer which was normal to the plane of the coil and which travelled over a circular scale graduated in degrees. The graphs show the intensity and direction fluctuations for the various evenings. In the data of May 25th and August 14th, where two sets of directional data were obtained, there is an actual correspondence only on some of the larger swings. The lack of correspondence in the smaller shifts is most probably due to the inability of the observers to follow these very rapid changes which were often of only a few seconds' duration.

In directional data obtained in this laboratory at the time of

FIG. 1.

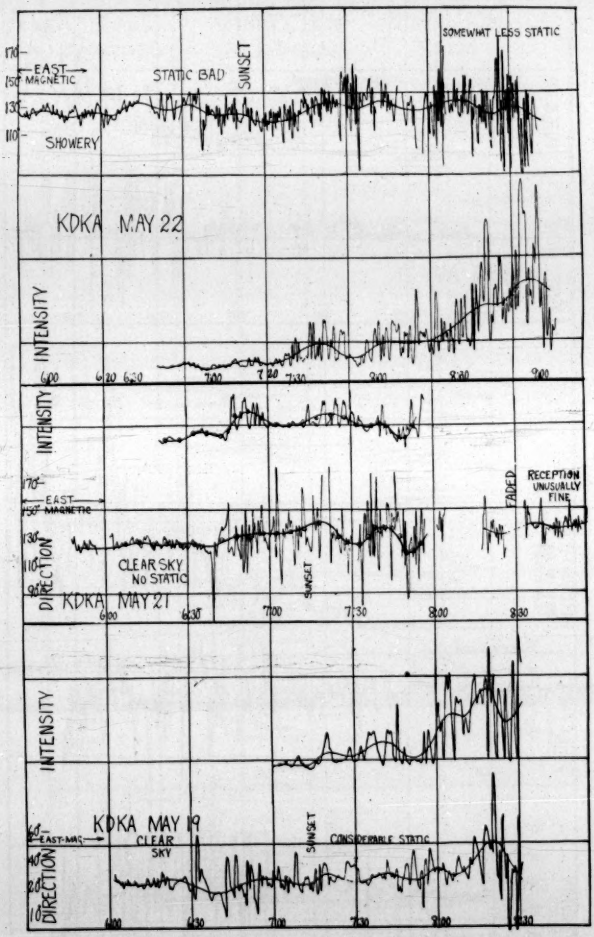

SOMEWHAT LESS STATIC
EAST
MAGNETIC
STATIC BAD
SUNSET
SHOWERY
KDKA MAY 22
INTENSITY
6:00
6:30
7:00
7:30
8:00
9:00
INTENSITY
DIRECTION
EAST
MAGNETIC
FADED
RECEPTION UNUSUALLY FINE
CLEAR SKY NO STATIC
SUNSET
KDKA MAY 21
6:00
6:30
7:00
7:30
8:00
8:30
INTENSITY
KDKA MAY 19
EAST-MAG
CLEAR SKY
SUNSET
CONSIDERABLE STATIC
DIRECTION
6:00
6:30
7:00
7:30
8:00
8:30

FIG. 2.

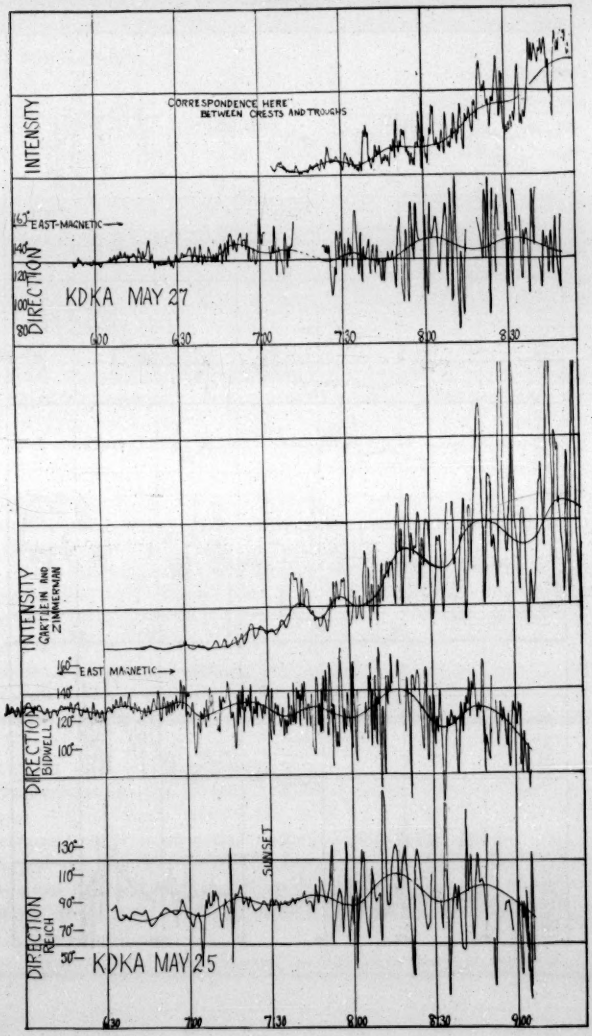
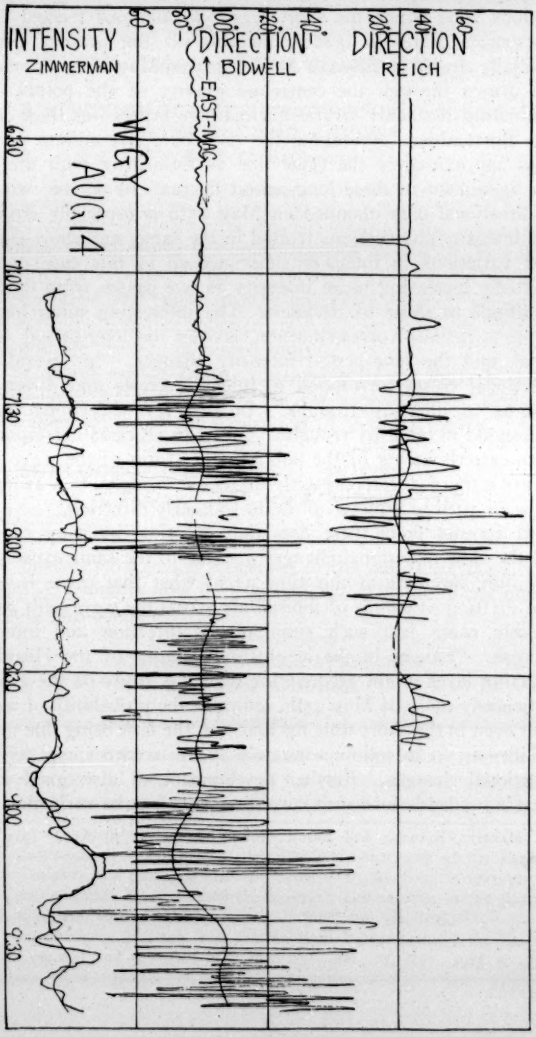

INTENSITY
CORRESPONDENCE HERE BETWEEN CRESTS AND TROUGHS
EAST-MAGNETIC
DIRECTION
KDKA MAY 27
6:00
6:30
7:00
7:30
8:00
8:30
INTENSITY
QUARTELLIN AND ZIMMERMAN
EAST MAGNETIC
DIRECTION
BIDWELL
SUNSET
DIRECTION
REICH
KDKA MAY 25
6:30
7:00
7:30
8:00
8:30
9:00

FIG. 3.


INTENSITY
ZIMMERMAN
DIRECTION
BIDWELL
DIRECTION
REICH
EAST-MAG
WGY
AUG 14
6:30
7:00
7:30
8:00
8:30
9:00
9:30

the January eclipse [1] there were remarked certain long-time fluctuations upon which the short erratic fluctuations seemed to be superposed. This is again noticeable on the present graphs, especially clearly on those of May 22nd and May 28th. A smooth line drawn through the centre of gravity of the points, thus eliminating the short erratic fluctuations, brings out these long-time fluctuations. Averaging the data over five-minute periods gives approximately the same line as estimating with the eye. The agreement in these long-period fluctuations of the two sets of directional data obtained on May 25th is especially striking. The intensity observations treated in the same way show similar slow variations in intensity superimposed in this case upon a gradually increasing mean intensity as one passes from daylight conditions to those of darkness. The interesting thing here is the quite definite correspondence between the long-period directional, and the long-period intensity changes. In several sets directional crests correspond to intensity crests and directional troughs to intensity troughs. In two sets directional crests correspond to intensity troughs. Crests in all cases corresponded to an easterly swing of the pointer or a swing of the wave path toward a more easterly-westerly direction; troughs, to a swing of the wave path to a more northerly-southerly direction.

It appears from these data that the slow intensity changes and the slow directional changes are due to the same cause. We may only speculate at this time as to what that cause is. The slow drifting of clouds of ionized air across the wave path would possibly cause just such simultaneous direction and intensity changes. Changes in the height and contour of the Heaviside reflecting layer might account for them. A study of the graphs, particularly those of May 25th, indicates the probability of agreement even in the short-time fluctuations, the lack being due to our inability as yet to follow accurately and to record completely the directional changes. Further development of directional apparatus is needed before such correspondence can be verified.

[1] MERRITT, BIDWELL and REICH: JOUR. FRANK. INST., April, 1925, **199**, p. 485.

NOTES FROM THE RESEARCH LABORATORY, EASTMAN KODAK COMPANY.*

A STUDY OF THE EFFICIENCY OF GUILLOTINE PAPER-CUTTING KNIVES.[1]

By I. C. Matthews.

[ABSTRACT.]

AN account is given of a detailed study of the comparative efficiencies of sandstone and emery-ground knives for the cutting of photographic paper. Photomicrographs are included, showing both sandstone and emery-ground knives at different periods of their use and the results obtained from sandstone wheels of different origin are given in tabulated form.

The quality of the cutting obtained with any knife is shown by photographs and the reason for the superiority of sandstone wheels is explained by an application of Beilby's theory.

TETRAIODOPHENOLPHTHALEIN SODIUM SALT.[2]

By H. T. Clarke, D.Sc., and E. E. Dreger, Ph.D.

[ABSTRACT.]

A DESCRIPTION of the properties of the salt ($C_{20}H_8O_4I_4Na_2 \cdot 3\frac{1}{2}H_2O$), which is now finding application in the X-ray examination of gall-bladder.

ASPHERICAL LENS SYSTEMS.[3]

By Ludwik Silberstein.

[ABSTRACT.]

THE properties of the Cartesian surfaces being first briefly recalled, a general method is given for constructing an aberrationless optical system of any number of such refracting surfaces.

* Communicated by the Director.

[1] Communication No. 248 from the Research Laboratory of the Eastman Kodak Company, and published in *Paper Trade Jour.*, **81**, Oct. 12, 1925, p. 50.

[2] Communication No. 245 from the Research Laboratories of the Eastman Kodak Company, and published in *Amer. J. Röntg.*, **14**, 341, 1925.

[3] Communication No. 243 from the Research Laboratories of the Eastman Kodak Company and published in *J. Opt. Soc. Am.*, **11**, Nov., 1925, p. 479.

As with each of these surfaces a new free parameter is introduced, it is shown how much parameters can be utilized for satisfying other requirements in addition to that of the freedom from aberration. In particular, a method is developed for satisfying, by a system of two Cartesian surfaces, the sine-condition up to terms of the fourth order and thus constructing an aplanatic lens properly so-called. In the last section it is shown how such a lens can be made achromatic by the insertion of a third surface, and the results here arrived at are illustrated on a complete numerical example.

The Size of the Uncharged Atom of Silver. F. BIELZ. (*Zeit. f. Physik.*, Vol. 32, No. 2.)—A small ray of silver atoms passed through an aperture into an atmosphere of nitrogen. There were collisions between the atoms of the metal and the molecules of the gas, so that the ray possessed fewer and fewer atoms the farther it was from the orifice. Three glass plates were exposed to the atomic stream, the silver there deposited was studied and from this the author deduces the important conclusion that the radius of the uncharged silver atom is one Ångström unit or 1.0×10^{-8} cm. Most other methods of arriving at the value of the radius give a larger result. G. F. S.

On the Electrification of Water, Snow and Other Solids by Fine Pulverization. H. KAEHLER and C. DORNO. (*Ann. d. Physik.*, No. 9, 1925.)—Since different experimenters on this subject have reached contradictory results, the authors went to Davos in the Engadine last winter with the purpose of examining carefully the matters in dispute. There, partly sheltered by the eaves of the observatory, they set up a Faraday cage with a volume of 1 cm. in a locality where the earth's electrical field was weak. In the cage were a polonium collector to measure the volume charge and, in addition, an insulated brass plate to measure the charge of whatever fell on it. They made experiments with atomized water, dry snow, with meals of various sorts, with ashes, sand and dust. "From our experiments it is evident that in most cases the very finest dust is negatively charged. . . . The electrification comes from a mechanical separation of a double layer of electricity on the surface of the body with the negative electricity outside." They found in agreement with Lenard that in finely divided water the large drops are positive and the very small ones negative. They made another attempt to detect an electrical charge produced by the vaporization of water but, like their predecessors, they could find no charge thus caused.

G. F. S.

NOTES FROM THE U. S. BUREAU OF CHEMISTRY.*

NARCOTIC AND TOXIC POTENCY OF ALIPHATIC ALCOHOLS UPON RABBITS.[1]

By J. C. Munch and E. W. Schwartze.

[ABSTRACT.]

THE toxicity of the lower aliphatic monatomic alcohols when administered by mouth has been determined. As the molecular weight increases the narcotic and toxic properties increase. In the case of most of the alcohols the narcotic properties increased more rapidly than the toxic properties. The results of this investigation are shown in the following table:

Narcotic and Toxic Potencies of Aliphatic Alcohols. Oral Administration to Rabbits.

Alcohol.	Average C.C. per Kg.		Mol. per Kg.		Ratio of Molar Potency EtOH-1.00.		Ratio $\frac{CLD}{MND}$.			
	MND	CLD	MND	CLD	MND	CLD	N-Primary.	Iso-Primary.	Secondary.	Tertiary.
Methyl...	7.5	18.0	0.1875	0.4500	0.50	0.48	2.4	..	..	..
Ethyl....	5.5	12.5	0.0545	0.2150	1.00	1.00	2.3	..	..	..
n-Propyl.	1.75	3.5	0.0236	0.0472	4.0	4.6	2.0	..	..	..
Isopropyl.	2.85	10.0	0.0380	0.1333	2.5	1.6	..	..	3.5	..
n-Butyl..	1.05	4.25	0.0115	0.0465	8.2	4.6	4.0	..	..	..
Isobutyl..	1.75	3.75	0.0191	0.0410	4.9	5.2	..	2.1	..	..
sec-Butyl.	1.25	6.0	0.0137	0.0655	6.9	3.3	..	..	4.8	..
tert-Butyl	1.80	4.5	0.0191	0.0480	4.9	4.5	..	..	..	2.5
Isoamyl...	0.875	4.25	0.0080	0.0391	11.8	5.5	..	4.9	..	..
sec-Amyl.	0.50	3.5	0.0046	0.0322	20.5	6.7	..	..	7.0	..
tert-Amyl	0.75	2.5	0.0069	0.0230	13.7	8.6	..	..	..	3.3

MND—Minimum narcotic dose.
CLD—Certain lethal dose.

An abstract of the literature on narcotic and toxic potency is given in the original article.

* Communicated by the Chief of the Bureau.

[1] Published in *J. Lab. and Clin. Med.*, St. Louis, 10 (Sept., 1925): 985.

THE NITROGEN DISTRIBUTION AND PERCENTAGES OF SOME AMINO ACIDS IN THE MUSCLE OF THE SHRIMP, PENEUS SETIFERUS (L.).[2]

By D. Breese Jones, Otto Moeller and Charles E. F. Gersdorff.

[ABSTRACT.]

A STUDY was made of the distribution of nitrogen and of the amino acid content of shrimp muscle. The finely ground muscle of fresh shrimp, *Peneus setiferus* (L.), was extracted at room temperature with 95 per cent. alcohol, and finally with ether. The air-dried extracted muscle consisted of a white, tasteless, and odorless, light, coarse powder, having the following percentage composition, calculated on an ash-free and moisture-free basis: C, 52.93; H, 6.33; N, 16.88; S, 1.55. Analysis of the muscle preparation by the Van Slyke method gave the following results expressed as percentages of the total nitrogen: Amide N, 8.13; humin N, 1.29; cystine N, 1.21; arginine N, 19.52; histidine N, 6.07; lysine N, 8.63. These figures, calculated as percentages of the corresponding amino acids in the ash-free and moisture-free muscle, gave the following values: Cystine, 1.75; arginine, 10.24; histidine, 3.78; lysine, 7.60. The following percentages of amino acids were obtained by colorimetric methods: Cystine, 1.78; tryptophane, 1.21; tyrosine, 4.88. Aspartic acid (6.98 per cent.) and glutamic acid (15.0 per cent.) were determined gravimetrically. The amino acid composition of shrimp muscle is compared with that recorded for scallop muscle.

PROTEINS OF TIMOTHY AND ORCHARD GRASS POLLEN AND THEIR RELATION TO VERNAL HAY FEVER.[3]

By F. A. Csonka, H. S. Bernton and D. B. Jones.

[ABSTRACT.]

IT IS now generally believed that hay fever is caused by the pollen of certain grasses and weeds blooming in the summer and fall. The pollen of timothy and orchard grass has been analyzed in the Bureau of Chemistry to ascertain which part produces hay fever. The results show that the protease fraction is the intoxicating and primary element in all hay fever subjects sensitive to timothy pollen, and that the albumin fraction is an added toxic factor in about half the subjects. The glutelin fraction is unimportant.

[2] Published in *J. Biol. Chem.*, **65** (1925): 59.

[3] Published in *Proc. Soc. Exper. Biol. and Med.*, **23** (1925): 14.

NOTES FROM THE U. S. BUREAU OF MINES, DEPARTMENT OF COMMERCE.*

PLASTIC MAGNESIA.

By O. C. Ralston, R. D. Pike, and L. H. Duschak.

MUCH detailed information on the production of plastic magnesia from magnesite mined near Chewelah, Wash., was accumulated during a coöperative investigation conducted by the Bureau of Mines and the Northwest Magnesite Company at the laboratories of the University of California in 1919–1921. This was supplemented by similar work with other magnesites, particularly those of California, in the endeavor to produce a plastic magnesia that would be satisfactory for making the so-called "Sorel" cement, composition flooring, stucco, and plasters. As standardized methods for testing such compositions did not exist, it was necessary to examine carefully the various methods in use and choose those that seemed appropriate. In consequence, the many tests made by the methods selected can be used for reference by those who wish to adopt standard methods of testing.

During the research it was found that if calcined magnesia containing free lime (CaO) were brought into contact with CO_2 gas at temperatures slightly above the dissociation temperature of magnesium carbonate, but below that of calcium carbonate, all of the free lime was rapidly converted to calcium carbonate with a rather large liberation of heat, while the magnesia remained unaffected. This reaction, which was termed recarbonation, was of such a quantitative nature and seemingly of such potential importance that much experimental work was done on it. Although the results of recarbonation of low-lime magnesites were not immediately visible, the effects on the products containing higher amounts of lime were very pronounced; even calcined dolomite gave a satisfactory product after it had been recarbonated in order to render the lime inert. Of course, this would make the dolomite consist of about 70 per cent. inert material, but since most of the cement mixtures used call for the addition of a rather large amount of inert material and an excellent cement can be made with 12 per cent. MgO, this matter is not important.

* Communicated by the Director of the Bureau of Mines.

For flooring about 40 per cent. MgO is used, consequently dolomite would not serve unless the usual mix were changed.

The research, therefore, arrived at a more or less unexpected conclusion. Originally undertaken to develop methods of making satisfactory plastic magnesia from the various magnesite deposits in the western states, it attained this object, but it also revealed that plastic magnesia of fair quality could be produced from dolomite, a material cheaply obtainable in the eastern states, where the market for plastic magnesia is the largest. If large-scale development of the process for treating dolomite proves successful, the deposits of magnesite in the western states will become less important, as far as the supplying of plastic magnesia is concerned. Further details are given in Bulletin 236.

GEORGIA AND ALABAMA CLAYS AS FILLERS.

By W. M. Weigel.

THE white clays or kaolins of Georgia and, to a small extent, of Alabama, have been utilized in the ceramic industry for many years. Some of these deposits have supplied clay to paper manufacturers and a very few have produced clay for use in rubber compounding and the manufacture of oilcloth and paint. As many owners and operators of clay deposits are unfamiliar with the different requirements for clays to be used as fillers, and so are unable to prepare their product for the market to which it is best adapted, the Bureau of Mines, in its endeavor to increase efficiency and economy in the mineral industries, has studied the clays in question to ascertain the uses to which they could be most efficiently put. A study of the Georgia clays for ceramic use was the subject of an earlier investigation by the Bureau of Mines.[1]

The principal manufactured articles in which clay is used as a filler or coating material are paper, wall paper, rubber, paint, oilcloth, textiles, kalsomine, plaster, and matches. For these uses, the clay must be white or nearly so, and in this investigation only the white clays or sedimentary kaolins were considered. It was found that many of the clays tested would be suitable for use,

[1] STULL, R. T., and BOLE, G. A., "Washing Tests of Georgia Clays," *Jour. Am. Cer. Soc.*, 6, June, 1923, pp. 730–741; "Refractory Possibilities of Some Georgia Clays," *Jour. Am. Cer. Soc.*, 6, May, 1923, pp. 663–673. BOLE, G. A., and STULL, R. T., "Use of Sedimentary Kaolins of Georgia in White Ware," *Jour. Am. Cer. Soc.*, 6, July, 1923, p. 854.

when properly prepared, for filler purposes. Additional data are presented in Technical Paper 343.

PROPERTIES OF TYPICAL CRUDE OILS FROM THE PRODUCING FIELDS OF THE WESTERN HEMISPHERE.

By A. J. Kraemer and L. P. Calkin.

For several years the Bureau of Mines has been engaged in a survey of typical crude oils from the producing fields of the United States. Results of these surveys have been published as Reports of Investigations. More recently, the Bureau has studied properties of crude oils from countries other than the United States, typical of the producing districts of Canada, Mexico, Trinidad, Venezuela, Argentina, Colombia, and Peru.

The Bureau of Mines undertook a study of foreign crude oils for two reasons: First, foreign fields are potential sources of supply for the United States; in fact, considerable quantities of some foreign crudes have already been imported. Second, these oils are very similar in physical and chemical properties to oils found in the United States and a study of these resemblances has scientific value.

Most of the samples were collected during the summer of 1922, although some samples date back to 1919 and 1920. The samples were placed in cans that were tightly soldered at once and there is no evidence that the oils had weathered before they were analyzed. All the samples are thought to be fairly representative of the districts under consideration.

The details of the methods used in this survey in collecting samples, making laboratory tests, and interpreting results, have been discussed in the reports on domestic crudes. For a detailed description of the tabulated results, the reader is referred to Technical Paper 346.

THE VAPOR PRESSURES OF THE COMMON METALLIC CHLORIDES AND A STATIC METHOD FOR MEASUREMENT AT HIGH TEMPERATURES.

By C. G. Maier.

The writer has completed a study undertaken primarily to furnish technical data on the vapor pressures and heats of vaporization of the metallic chlorides at high temperatures. Persons

interested in such figures do not need to be reminded of the inadequacy of the data found in the usual handbooks.

In the past, study of the fundamentals of certain important metallurgical processes dealing with chlorides at high temperatures has been difficult, especially the chloridizing roast and chloride volatilization. One important reason for the difficulty has been the almost complete lack of vapor-pressure and thermal data that were technically usable. Such data are not only necessary to understand losses or vaporization of metals as chlorides, but they are essential to deal quantitatively with the chemical reactions that occur in the processes mentioned above.

The static method which has been used for the determinations was developed at the Salt Lake laboratories of the University of Utah and the bureau. By this method many points of a vapor-pressure curve could be found during the course of a single satisfactory experiment.

The method will determine vapor pressures up to 1250° C. The method is static and direct, and involves no assumptions relative to the behavior of the vapor according to the gas law. The vapor pressures of the commoner metallic chlorides have been determined over this range. Available data on the vapor pressures and decomposition pressures, of boiling-points, and heats of vaporization of the common metallic chlorides were calculated from the vapor-pressure data. Further details are presented in Technical Paper 360.

The Partial Tones of a Struck String. Part I. Experimental Investigation of the Fundamental. W. H. GEORGE. (*Phil. Mag.*, Aug., 1925.)—The shadow of the middle point of the struck string was optically projected upon a moving photographic plate and the record of the motion of the point thus got was analyzed by a Mader Harmonic Analyzer. The tension and length of the string were maintained constant as was the velocity with which the hammer impinged on the string. With the heaviest metallic hammer used no less than seven positions were found, as the striking point was shifted from one end to the other, at which the amplitude of the fundamental was a maximum. With the lightest hammer only two maxima were detected. The greatest amplitude of the fundamental was obtained by striking the string near a bridge, and the heavier the hammer is the nearer to the bridge is this point. G. F. S.

THE FRANKLIN INSTITUTE.

(Proceedings of the Stated Meeting, Wednesday, December 16, 1925.)

THE meeting was called to order by President Wm. C. L. Eglin, at eight-nineteen P.M.

The President called for the reading of the minutes of the previous meeting. The Secretary announced that the minutes had been published in full in the December number of the JOURNAL and moved that they be approved as printed. The motion was adopted.

Under the report from the Board of Managers, the Secretary presented as the first item of business the proposed amendment to the By-laws concerning membership. He announced that notice had been given at the October meeting of the amendment which would be presented at this time, and read the changes which were suggested. He stated that the By-law as amended had been printed in the November number of the JOURNAL and pointed out that the essential changes suggested were the institution of a new class of membership, to be known as "Student Membership," and a reformulation of the statement of privileges of membership. These amendments are shown in the following two sections:

Section 8. Student members shall be over sixteen and under twenty-two years of age. They shall pay annual dues of three dollars if they do not receive the JOURNAL of the Institute, and six dollars if they do receive the JOURNAL. The term of student members shall be limited by the age of twenty-two years, after which time they shall be eligible for transfer to the other types of membership upon the payment of the appropriate fee or dues.

Section 9. Privileges: All members, of whatever class, are entitled to participate in the meetings of the Institute, in the use of the Library, to receive tickets for the lectures, and to receive monthly one copy of the JOURNAL of the Institute, except that student members, and honorary and corresponding members shall not have the right to vote, nor to hold office, and student members paying the three-dollar annual dues shall not receive the JOURNAL of the Institute.

The meeting then adopted the amended article—Article II, Members—unanimously.

The Secretary reported for the information of the Institute that since the last stated meeting there had been a gain of membership of thirteen, with a loss of two by death. He announced with sincere regret the death of J. Edward Eyanson and John D. McIlhenny.

Under the heading of "Nomination of Officers and Members of the Board of Managers," the following nominations were presented in writing:

President: Dr. William C. L. Eglin—for one year, nominated by Dr. Walton Clark, Mr. W. H. Fulweiler, Prof. James Barnes.

Vice-president: Mr. C. C. Tutwiler—renominated for a period of three years, nominated by Mr. Nathan Hayward, Mr. M. S. Morgan.

Vice-president: Mr. Walton Forstall—for one year, to fill the vacancy caused by the resignation of Dr. Gellert Alleman, nominated by Mr. Benjamin Franklin, Mr. Henry Howson.

Treasurer: Mr. Benjamin Franklin—for one year, nominated by Mr. W. H. Fulweiler, Prof. James Barnes.

Board of Managers: For full term—Prof. James Barnes, Mr. George H. Benzon, Jr., Mr. G. H. Clamer, Mr. Theobald F. Clark, Prof. Arthur W. Goodspeed, Mr. Charles Penrose, Dr. George D. Rosengarten, Prof. William Chattin Wetherill. Also Mr. F. J. Chesterman—for two years, to fill the vacancy caused by the death of Mr. Charles A. Hexamer, nominated by Dr. Walton Clark, Mr. James S. Rogers.

The President called for further nominations. There being no further nominations, upon motion, the nominations were closed.

On behalf of the Committee on Science and the Arts, Mr. S. B. Eckert, Chairman of the Sub-committee which made the investigation, presented Mr. Thomas Midgley, Jr., as the recipient of the Longstreth Medal for the invention of a novel and ingenious optical indicator. The certificate of award and the Medal were presented to Mr. Midgley by the President of the Institute.

The President then presented as the speaker of the evening Prof. Robert W. Wood, Professor of Experimental Physics in Johns Hopkins University, who spoke on the "Optical Excitation of Metallic Spectra."

The meeting adjourned, with a rising vote of thanks to Professor Wood for his brilliant paper, at ten-eight P.M.

HOWARD MCCLENAHAN,
Secretary.

COMMITTEE ON SCIENCE AND THE ARTS.

(Abstract of Proceedings of Stated Meeting held Wednesday, December 2, 1925.)

HALL OF THE COMMITTEE,

PHILADELPHIA, December 2, 1925.

MR. HAROLD CALVERT *in the Chair.*

The following reports were presented for final action:

No. 2825: Hilger Interferometer.

The object of this invention is to provide a simple and accurate method for locating and correcting imperfections in prisms and lenses, which may be due to faults of workmanship, to faults such as spherical aberration, astigmatism, distortion, etc., and to faults due to lack of homogeneity in the glass or other substance of which the optical element is made.

The apparatus used for the above purpose resembles in form the well-known Michelson interferometer in which a beam of monochromatic light, such as that obtained from a mercury-vapor lamp combined with suitable filters, is divided into two parts. One part is passed twice through the optical element under test and then recombined with the other part in such a way as to produce a set of interference bands which arrange themselves in what the inventor

calls a "contour map" of the imperfections. The workman preferably draws this map with a brush filled with rouge upon the surface under treatment and then removes the superfluous material from the prominences in the ordinary manner.

In consideration of the great scientific value of this instrument for the testing of optical devices, the Committee recommended the award of the John Price Wetherill Medal to Mr. Frank Twyman, of London, England.

No. 2829: Midgley Optical Indicator.

This device is a high-speed indicator intended for use with automobile and aeroplane engines, and it can be used to give either a qualitative or a quantitative result.

These results are in the form of diagrams in which the pressure is plotted against the positions of the piston, called the pressure-volume diagram or against the crank angle, called the pressure-time diagram. In the optical system a beam of light from an incandescent bulb strikes upon a mirror, the position of which is determined by the position of the piston in the cylinder. It is then reflected to a rotating mirror, the position of which depends upon the second element required, from which it is again reflected to a translucent screen for observation of a single cycle, or to bromide paper for a permanent record.

There are a number of features in this device that are of value in making it a reliable instrument for determining the condition of operation in the cylinder of an internal combustion engine by obtaining both a visual and a photographic record of the relation between the time and pressure and the time and volume, thus furnishing the required information concerning the movement of the piston for the entire double stroke. Among these may be mentioned the method of securing synchronism between the movement of the piston and that of the motor operating the rotating mirror; the use of an optical system by means of which the reciprocating movements of the piston and the oscillations of a mirror controlled by it are delivered to a screen in the form of a continuous curve and the method by which during the time of a photographic exposure, the electric bulb furnishing the source of light is made to give a much higher candle power by being fed with excess voltage. The substitution of a piston and spring for a diaphragm in the pressure element of this instrument is also a distinct advantage since it gives a uniform scale for the entire height of the pressure card, whereas the diaphragm necessitates the use of a special scale.

In consideration of a novel method of reducing the inaccuracies due to inertia in devices mechanically controlled, of the adaptation of this device to an easily scaled time-pressure card and of the introduction of the revolving mirror for this purpose, the Committee recommended the award of the Edward Longstreth Medal to Mr. Thomas Midgley, of Dayton, Ohio.

The following reports were presented for first reading:

No. 2837: Hydraulic Regulating Valve.

No. 2839: Shooting Iron.

GEO. A. HOADLEY,
Secretary to Committee.

MEMBERSHIP NOTES.

ELECTIONS TO MEMBERSHIP.

(Stated Meeting, Board of Managers, December 9, 1925.)

RESIDENT MEMBERS.

MR. TALBOT MERCER ROGERS, Student, Haverford, Penna., and for mail: 7 E. M. Witherspoon Hall, Princeton, N. J.

NON-RESIDENT MEMBERS.

LIEUTENANT-COMMANDER MARION EPPLEY, PH.D., Scientist, Eppley Laboratory, Newport, R. I.

PROFESSOR H. E. REILLEY, Professor of Physics, McGill University, Montreal, P. Q., Canada.

CONTRIBUTING MEMBERSHIP.

E. G. Budd Manufacturing Company:
EDWARD G. BUDD, JR., 517 Ellet Street, Germantown, Penna.
COLEMAN B. MOORE, 414 Berkley Road, Haverford, Penna.

Bell Telephone Company:
MR. B. H. STEVENS, 261 North Broad Street, Philadelphia, Penna.

CHANGES OF ADDRESS.

DR. F. W. FRERICHS, 4557 West Pine Boulevard, St. Louis, Mo.

MR. W. S. SLOATMAN, Supervisor, Tuckahoe, N. J.

MR. C. F. SULZNER, 1006 Henrietta Towers, Miami, Fla.

MR. EDWARD H. TAIT, Virginville, Penna.

DR. C. C. THOMAS, 310 Union Oil Building, 617 West Seventh Street, Los Angeles, Calif.

MR. ROBERT V. TOWNEND, Department of Chemistry, University of Delaware, Newark, Dela.

MR. HARRY R. VANDEVENTER, 59 Washington Square, South, New York City, N. Y.

MR. EDWARD L. ZIESEL, 1917 East Cumberland Street, Philadelphia, Penna.

NECROLOGY.

Dr. Edward Goldsmith died at his home 658 North Tenth Street, Philadelphia, on November 15, 1925.

He was born in Germany in 1833, where he received his education. He came to the United States when he was twenty-five years old and obtained a position with Powers and Weightman as analytical chemist. He was in the service of this company for fifty years. Since his retirement from active work he has devoted his time to mineralogy and chemistry and to the making of a collection of minerals containing many rare specimens. He was a member of several scientific societies and was intensely interested in all fields of modern progress.

Doctor Goldsmith was greatly afflicted in his later years by a partial or complete loss of his sight. In spite of this well-nigh insuperable obstacle to

scientific attainment, he maintained his keen interest in scientific things to the end of his life and was a faithful attendant upon scientific exercises.

He became a member of The Franklin Institute on January 16, 1884; he was active on the Committee on Science and the Arts for fifteen years and was its Chairman during the term 1905–1906. He was a member of the Board of Managers from 1908 to 1916.

Mr. J. Edward Eyanson, 207 South Tenth Street, Philadelphia, Penna.

LIBRARY NOTES.

RECENT ADDITIONS.

ABBOT, C. G.—The Earth and the Stars. 1925.

ALLEN, H. STANLEY.—Photo-electricity. Second edition. 1925.

American Electrochemical Society.—Transactions. Vol. 47. 1925.

American Petroleum Institute.—American Petroleum Supply and Demand. 1925.

American Public Health Association.—Standard Methods for the Examination of Water and Sewage. Sixth edition. 1925.

American Public Health Association and Association of Official Agricultural Chemists.—Standard Methods of Milk Analysis. Fourth edition. 1923.

Anniversary Volume Dedicated to Prof. Hantaro Nagaoka by His Friends and Pupils on the Completion of Twenty-five Years of His Professorship. 1925.

BEERY, PAULINE G.—Chemistry Applied to Home and Community. 1923.

BERG, RAGNAR.—Vitamins: A Critical Survey of the Theory of Accessory Food Factors. Translated from the German by Eden and Cedar Paul. 1923.

CARPENTER, FRANK G.—Java and the East Indies. 1923.

CASE, JOHN.—The Strength of Materials. 1925.

CRUESS, W. V., and CHRISTIE, A. W.—Laboratory Manual of Fruit and Vegetable Products. 1922.

D'ALBE, E. E. FOURNIER.—The Moon-element: An Introduction to the Wonders of Selenium. 1924.

ELLIOTT, C.—Distillation in Practice. 1925.

ENGLER, C., and HOEFER, H. VON.—Das Erdöl. Vol. 6. 1925.

Faraday Society.—Investigation on Oppau Ammonium Sulphate-nitrate. 1924.

First World Power Conference, 1924.—Transactions, 5 volumes. No date.

GARARD, IRA D.—Applied Chemistry. 1924.

GARDNER, WILLIAM.—Chemical Synonyms and Trade Names. Second edition. 1925.

GELPI BLANCO, JUAN.—Aprovechamiento de las Energías Naturales. 1924.

HAMILTON, ALICE.—Industrial Poisons in the United States. 1925.

HARDY, A. C.—Motorships. 1925.

HOLMAN, RICHARD M., and ROBBINS, WILFRED W.—A Textbook of General Botany for Colleges and Universities. 1924.

HOWE, H. E. (Editor).—Chemistry in Industry. Two volumes. 1924–1925.

HUTCHESON, T. B., and WOLFE, T. K.—The Production of Field Crops. 1924.

INGLE, HERBERT.—Elementary Agricultural Chemistry. Second edition revised. 1913.

KINGZETT, C. T.—Chemical Encyclopædia. Third edition. 1924.
LEVENE, P. A.—Hexosamines and Mucoproteins. 1925.
LEVI, GEORGES.—La Technique du Pétrole. No date.
MCCANDLISH, ANDREW C.—The Feeding of Dairy Cattle. 1922.
MCCOLLUM, E. V., and SIMMONDS, NINA.—The Newer Knowledge of Nutrition. Third edition. 1925.
MAHIN, EDWARD G.—Quantitative Analysis. Third edition. 1924.
Mineral Industry during 1923 and 1924. Vols. 32 and 33. 1924–1925.
MOORE, F. J.—Outlines of Organic Chemistry. Third edition. 1924.
NOWAK, CARL A.—Non-intoxicants. 1922.
Organic Syntheses. Vols. 4 and 5. 1925.
OSBORN, CHASE SALMON.—Madagascar, Land of the Man-eating Tree. 1924.
PETERS, FREDUS N.—Applied Chemistry. 1922.
PHILLIPS, EVERETT FRANKLIN.—Beekeeping. 1923.
Poor's Railroad Section, 1925. 1925.
POPE, KATHERINE.—Hawaii: The Rainbow Land. 1924.
PRINGSHEIM, HANS.—Zuckerchemie. 1925.
RAYLEIGH, ROBERT JOHN STRUTT, Fourth Baron.—John William Strutt, Third Baron Rayleigh. 1924.
RECTOR, THOMAS M.—Scientific Preservation of Food. 1925.
SADTLER, SAMUEL P., COBLENTZ, VIRGIL, and HOSTMANN, JEANNOT.—Textbook of Chemistry Intended for the Use of Pharmaceutical and Medical Students. Fifth edition. 1918.
SANDERS, T. H.—Laminated Springs. No date.
SCOTT, WILFRED W., and Others.—Standard Methods of Chemical Analysis. Fourth edition. 1925.
SMITH, J. RUSSELL.—North America. 1925.
SMITH, J. RUSSELL.—The World's Food Resources. 1919.
SNODGRASS, R. E.—Anatomy and Physiology of the Honeybee. 1925.
Société Française de Photographie and le Photo-Club de Paris.—XIXe Salon International de Photographie. 1924.
SPOONER, HENRY J.—Machine Design, Construction and Drawing. Fifth edition. 1924.
SWINDIN, NORMAN.—Modern Theory and Practice of Pumping. 1925.
THOMAS, STANLEY.—Bacteriology. 1925.
TRINKS, W.—Industrial Furnaces. Vol. 2. 1925.
TUTTLE, LUCIUS, and SATTERLY, JOHN.—The Theory of Measurements. 1925.
WHITNEY, MILTON.—Soil and Civilization. 1925.

BOOK REVIEWS.

NUEVA TEORIA CÓSMICA Y SU APLICACIÓN A LAS CIENCIAS NATURALES. By Mariano N. Ruiz. 253 pages, small 8vo. Comitan, Chiapas, Mexico, 1925.

The promulgator of a new cosmic theory has no easy road. Cosmogonies have arisen and passed away in considerable number since the dawn of written history, and we do not have the primitive man's idea of the universe. Time was when the most intelligent and best educated of civilized men were perfectly sure that the earth was the centre of the universe. The book in hand is quite an extensive presentation of a theory of the origin and course of the cosmos

under the influence of the Newtonian theory of gravitation. The author speaks of this theory in the most approving terms. He calls it a "grand and colossal fact" and one of the greatest discoveries that can be credited to human ability. He does not accept the doctrine of relativity in the form that its proponent gives it, nor does he accept the Laplace hypothesis. Undoubtedly there is a sort of fascination in the view that the Newtonian law (that every particle of matter attracts every other particle in the direct ratio of the mass and the inverse ratio of the square of the distance) may extend throughout space and be true of the most minute atom as well as of the largest star. Yet the phenomena of chemistry do not bear out the supposition. Electrical attraction seems to hold sway in the atomic areas. Modern chemists recognize in the atom an association of positive and negative foci with which the simple law of gravitation does not operate. It is true that a distinguished American physicist lately lectured at The Franklin Institute on the "Astronomy of the Atom," but it does not appear that he taught that the sun's family is merely a set of large electrons. In fact, Millikan has pointed out that electrons may shoot "madly from their spheres," but so far as human knowledge goes the planets and satellites of our system have kept their appointed places. Our author's view of the water molecule exemplifies his tendency to compare the minute with the great, for he says that in water we have an oxygen atom around which cavort (a cuyo alrededor giran) two hydrogen "planets." It might be better to call them satellites. This view is repeated on p. 246 in a footnote. Yet it is not the one usually assumed by chemists. That there is motion of the atoms forming a mass, elementary or compound, is admissible, but the general idea is a to-and-fro motion and not a revolution. Moreover, those who seek to compare either the atom itself or associations of atoms as analogous to the cosmos, must bear in mind that, so far as astronomy indicates, our solar system is unique; no other similar aggregation has been observed. Rotating systems are numerous, but they consist of a few stars, mostly a pair rotating about a common centre of gravity, presumably within the mass of one member of the system. A central luminary of overwhelming mass around which rotates a series of masses, themselves attended by one or more minor masses, is not yet observed in any other part of the universe. We must not say that such a condition is not duplicated, but we certainly do not yet know of such. The familiar phenomenon of double stars is not analogous to our system.

Señor Ruiz seems to accept the principle of gravitation as thoroughly established, but it has been challenged of late years, and there are some who think that the fall of a body to the earth is not due to *vis a fronte*, but to *vis a tergo*.

The subject is too abstruse for full discussion in a review.

HENRY LEFFMANN.

INVESTIGATION ON OPPAU AMMONIUM SULPHATE-NITRATE. Reprinted from the Transactions of the Faraday Society, No. 58, Vol. 20, part 1, July, 1924. 32 pages, 8vo, paper. Price, 3 shillings.

This is a report of an extensive and elaborate investigation of the physical and chemical properties of the fertilizer salt manufactured at the Oppau plant of the BASF by mixing ammonium sulphate and ammonium nitrate in the

proportion of one molecule of the former to two of the latter. The importance of the investigation lies in the fact that the store of this salt was alleged by German authorities to be the source of the violent explosion at the plant on September 21, 1921. The data of the report are of such interest and value that an abstract has been prepared, which will be found elsewhere in this issue (page 140).

HENRY LEFFMANN.

HEXOSAMINES AND MUCOPROTEINS. By P. A. Levine, Rockefeller Institute for Medical Research. viii–163 pages, 8vo, boards. New York, Longmans, Green and Company, 1925. Price, $3.75.

This is one of the monographs on biochemistry edited by Doctor Plimmer, a series which has for some years been favorably known to biochemists and physiologists. The problems of life are essentially chemical and chemico-physical, even though a numerous section of scientists still assert that vital action cannot be reduced to the terms of the laboratory. The volume in hand introduces the reader to one of the most abstruse fields of biochemistry. The hexosamines are, as the name suggests, substances having the aliphatic structure of the sugars with the introduction of amine groups. For every hexose five hexosamines are possible, but up to the present time natural products are only 2-amino-derivatives. More complex forms have been prepared synthetically. The first compound of the type was discovered in 1878 by Ledderhose, who obtained from it chitin, a constituent of certain insect tissues. The exact structure of the compounds was a matter of dispute until Fischer and Leuchs produced it synthetically from arabinose, and thus its relation to glucose was established. For a while all hexosamines found in tissues were regarded as chitosamine, but distinctions have now been made. Chondrosamine, for instance, is obtained from mucoproteins of cartilage and tendon. So far it is not known if it is present in plant tissue or those of the lower animals. Levine thinks that chondrosamine may be found to be as widely distributed as chitosamine.

The mucoproteins, to which the second part of the book is devoted, are, as the name indicates, related closely to the proteins and are found in mucus but by no means limited to such secretions. They differ from the standard proteins in certain chemical reactions, such as being precipitable by dilute acetic acid and by forming more viscous solutions with water than ordinary proteins do. Indeed, common experience suggests that some forms of mucus are almost of a tissue nature. From a table of analyses of different kinds it is seen that carbon, hydrogen, nitrogen and oxygen are always present and sometimes sulphur. A carbohydrate grouping exists in these substances, stated to be in the form of a polysaccharide radicle. Experimental methods for preparing some of the substances are given in detail. Biochemists will find the work very useful, furnishing the most recent information on an important field in chemistry.

HENRY LEFFMANN.

ZUCKERCHEMIE. By Dr. Hans Pringsheim, University of Berlin, with collaboration of Dr. Jesaia Leibowitz. xii–322 pages, 8vo. Leipzig, Akademische Verlagsgesellschaft, m.b.H., 1925. Price, 16 marks.

This book is devoted to the pure chemistry of the sugars, not dealing with the analytic or technical phases. It is a very thorough and well-expressed compilation of the present knowledge of the molecular arrangements and interrela-

tions of this extensive and important group of carbohydrates. It is to Emil Fischer that we owe the largest amount of information concerning the peculiar aliphatic structure of the group, and the particular reactions between many of them and the phenylhydrazine compounds. One of the sugars being a natural product of immense importance in the food supply of the world, attention was, of course, early attracted to the study of its nature, but it was a long while before definite data were obtained. The property of rotating the plane of polarized light possessed by most of the group offered methods for quantitative determination which otherwise might have been one of the most difficult problems of routine proximate analysis. The relation of some of the natural products to the formation of alcohol brought about not only important chemical problems, but wide-spread social questions, still in seething condition.

It is somewhat astonishing to learn from the preface that ten years have elapsed since a comprehensive treatise has appeared in German on the subject of the constitution and relations of the sugars. Considering that, as remarked above, it was in Germany that the most illuminating work was done in this field, one would suppose that the literature there would be active. It is true that much information on the subject is to be found in comprehensive text-books, but thorough treatment, in which the extensive periodical literature is abstracted and summarized, can only be accomplished by means of special works. Such is the task that Doctor Pringsheim and his collaborator set before themselves and it has been well carried out. It may be a question whether some of the detail about the nature of the effects of polarized light needed so much explanation. Those who use the book must be well-trained chemists and have a good knowledge of the nature of polarization, so that the fundamental data regarding such phenomena may be omitted.

There is much of interest in connection with the section on the alcoholic fermentation. This phenomenon has been familiar to the human race since the earliest period of which we have definite record. For many centuries, indeed, up to a period within the memory of the old living chemists, it was regarded as "spontaneous," a term essentially understood as meaning without definite chemical action, but modern research has fully established its dependence on living organisms through the intermediation of enzyms. Reference is made to the work of Buchner and others in which fermentation is carried on by the catalytic action of the enzyms alone. Incidentally, Doctor Pringsheim states that yeasts may be developed to a degree of fermentive capacity that they do not normally possess, by certain conditions of growth. This is merely one of many thousands of instances now known of the operation of natural selection. In the case of the fermentation of grape juice, the acidity of the solution acts as protection against many accessory organisms, while the yeast, capable of growing in the acid liquid, decomposes the sugar. It would seem possible, however, to cultivate this same yeast to a form which would grow in feebly alkaline solution.

Chemists who desire a thorough discussion of the sugars in their interrelations as well as in their intimate structure, will find this book a most satisfactory aid. The German is exceptionally clear and direct, the references are comprehensive and carry the year as well as the volume; they are, as might be expected, largely to German publications. The publisher has done full justice to the work.

HENRY LEFFMANN.

STANDARD METHODS OF CHEMICAL ANALYSIS. By Wilfred W. Scott, Sc.D., University of Southern California, in collaboration with many specialists. Fourth edition, two volumes, 8vo. Vol. 1, The Elements, xxxviii–745 pages, and index. Vol. 2, Special Methods, xxviii–802 pages, and index. New York, D. Van Nostrand Company, 1925. Price, $12.

A work which has reached a fourth edition needs no special comment as to its general merits; its sale shows that it has met a wide demand satisfactorily. This book represents the labors of many specialists and consequently may be expected to give up-to-date procedures in all sections. Analytic chemistry is probably the least dynamic phase of the science. There is, indeed, much activity in the research into analytic methods. Chemical journals devote much space to new methods, but certain practical conditions restrict the adoption of these often for a long while and even may pass them over permanently. This is due to the extended development of the "authorized" and "official" methods, definite procedures which all chemists are obliged to follow. In food analysis, the introduction of official methods has been very extensive. The system was, indeed, introduced in that field at an early date, the British "Society of Public Analysts" having had a large part in originating the plan. In the United States the processes of the A.O.A.C. have dominated food, feed and fertilizer analysis for many years.

Confident, then, that this work will prove in the great mass of cases a perfectly safe guide for the analyst, something may be said as to its form and method, for after all, it is not all of text-book making to record data and describe procedures. In some respects the book does not appeal to the reviewer's taste. There seems to be a great deal of unnecessary matter. In the first volume there are fifteen pages of "contents" and in the second volume twelve. A table of contents is a useful addendum, but it should cover only the salient points; details are for the index. An extended table is especially inappropriate in this book, for the elements are treated in alphabetic order (an excellent plan) and the user can turn at once to the subject on which he wishes information. There is a good index, separately paged in each volume, covering both volumes, which is also a commendable feature. With each element are given physical data, which are hardly necessary for the users of the book. The sp. gr., m.p. and b.p. of sodium, for instance, are of no interest to the general analyst. Such data are for works on descriptive chemistry. It is true that but little space is taken up by such notes, but in the mass their insertion adds to the cost of printing. It is curious to note that while each paragraph relating to a quantitative method is headed "estimation," the word "determination" is used in the initial sentence. The spelling "nitrobenzine" is noted twice in one paragraph. This may be a typographic error, which is excusable in so large a book, but technicians are often indifferent to the rules of chemical nomenclature. In the chapter on the analysis of fats and oils, the Reichert-Meissl procedure for volatile acids is alone given, notwithstanding the fact that American chemists are using the glycerol-soda method, which is among the official methods of the A.O.A.C. and exclusively official in some foreign countries. In a paragraph concerning the quality of glass for certain operations several well-known resistance glasses are mentioned but "pyrex" is not in the list.

HENRY LEFFMANN.

PHOTO-ELECTRICITY: The liberation of electrons by light. By H. Stanley Allen, M.A., D.Sc., F.R.S.E. Second edition, with diagrams. xi–320 pages, 8vo. New York, Longmans, Green and Company, 1925. Price, $6.50.

The professional title of the author of this book carries one back a half a century, for he is "Professor of Natural Philosophy" in the University of St. Andrews. Most English-speaking persons have long since substituted "physics" for "natural philosophy" as a title for that branch of science which deals with forms of energy, now, it is true, rapidly absorbing chemistry and being itself absorbed into mathematics. Yet many teachers are now living who remember the catalogues of "Mathematical and Philosophical Instruments," issued by the firms who supplied lecture and research material to our schools and colleges. Taine refers with some sarcasm to the survival of the term by saying, "In England, a barometer is still called a philosophical instrument."

The present work, being a second edition, needs no extended review. Between the two issues an eventful dozen of years has elapsed, marked not only by the great War, but by many epoch-making advances in both theory and practice of physical science. The quantum theory, the principle of relativity, the experimental work of Rutherford, Moseley and the Braggs, the extension of study on ultra-violet light, and the expansion of colloid chemistry are among the most important of these progresses.

Photo-electricity means in a general sense any electrical effect due to light, but in this work it is used in a more restricted sense to mean a change in the state of electrification induced by the action of light. Ultra-violet radiation is the more active form and hence the term "actino-electricity" is sometimes used. The change by which selenium becomes a better conductor when illuminated—a peculiar action that has been long known—is strictly not within the compass of the work, although it is noted in the proper place. The greater portion of the text is of an abstruse nature, but a vast amount of information has been accumulated. The bibliography is quite extensive and those who are not familiar with the subject will be astonished at the bulk of literature available and the number of workers in the field. Two topics that find a wider interest than the recondite phases of the subject are fluorescence and phosphorescence and the problem of the latent image. The first recorded observation of fluorescence appears to be due to Boyle, who observed the effect in connection with an infusion of the wood of a tropical tree. Brewster noted the effect with chlorophyl and Herschel that with quinine solutions. Many years ago a comprehensive examination of the phenomena was made by Stokes. Phosphorescence is also discussed. The chapter on the latent image reviews the now extensive literature on the subject. The nature of the impression upon which the development of ordinary silver halide emulsions depends is still a matter of dispute. Not sufficient attention seems to be paid to the fact that the whole of the silver salt may be removed and yet the picture developed perfectly when a gelatine plate and thiosulphate are used.

The text and make-up of the book are excellent. It is one of a series of "Monographs on Physics" edited by Sir J. J. Thomson and Dr. Frank Horton.

HENRY LEFFMANN.

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS. Report No. 217, Preliminary Wing Model Tests in the Variable Density Wind-tunnel of the National Advisory Committee for Aeronautics. By Max M. Munk. 15 pages, illustrations, quarto. Washington, Government Printing Office, 1925. Price, ten cents.

This report contains the results of a series of tests with three wing models. By changing the section of one of the models and painting the surface of another, the number of models tested was increased to five. The tests were made in order to obtain some general information on the air forces on wing sections at a high Reynolds Number and in particular to make sure that the Reynolds Number is really the important factor, and not other things like the roughness of the surface and the sharpness of the trailing edge.

The few tests described seem to indicate that the air forces at a high Reynolds Number are not equivalent to respective air forces at a low Reynolds Number (as in an ordinary atmospheric wind-tunnel). The drag appears smaller at a high Reynolds Number and the maximum lift is increased in some cases. The roughness of the surface and the sharpness of the trailing edge do not materially change the results, so that we feel confident that tests with systematic series of different wing sections will bring consistent results, important and highly useful to the designer.

PUBLICATIONS RECEIVED.

The Alkali Industry, by J. R. Partington. 344 pages, illustrations, 8vo. New York, D. Van Nostrand Company, 1925. Price, $4.

Laboratory Exercises in General Chemistry, by Wm. Foster and H. W. Heath. 186 pages, illustrations, 8vo. New York, D. Van Nostrand Company, 1925. Price, $1.25.

Allen's Commercial Organic Analysis. Vol. 4 of the fifth edition. 648 pages, illustrations, 8vo. Philadelphia, P. Blakiston's Son and Company, 1925. Price, $7.50.

The Bureau of Standards: Its History, Activities and Organization, by Gustavus A. Weber. xv–299 pages, 8vo. Baltimore, The Johns Hopkins Press, 1925. Price, $2.

Wasserkraft—Jahrbuch 1924. 612 pages, illustrations, plates, 8vo. München, Richard Pflaum, 1925. Price, 24 gold marks.

La Concentration en Ions Hydrogène de l'eau de Mer le pH, by R. Legendre. vii–291 pages, illustrations, 8vo. Paris, Les Presses Universitaires de France, 1925. Price, 30 francs.

Gas Dampf und Flüssigkeit, by Hans von Jüptner. 61 pages, tables, 8vo. Leipzig, Otto Spamer, 1925. Price, 5 gold marks.

Wassermessungen bei Wasserkraftanlagen, by L. A. Ott. 282 pages, illustrations, 8vo. München, Richard Pflaum, 1925.

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On the Origin of the Auroral Green Line 5577 Å., and Other Spectra Associated with the Aurora Borealis. J. C. MCLENNAN and G. M. SCHRUM. (*Proc. Roy. Soc.,* A747.) **The Luminescence from Solidified Gases down to the Temperature of Liquid Hydrogen and Its Application to Cosmic Phenomena.** L. VEGARD. (Communications from the Physical Lab. of the Univ. of Leyden, No. 175.)—The source of this green line has been much discussed in the last two or three years. In the first of these papers it seems to be definitely located. There is reason to believe that the upper atmosphere is rich in helium. With this in mind McLennan and Schrum at Toronto took up the study of the electric discharge through this constituent of the atmosphere. They used a discharge tube 1 inch in diameter and 30 feet long. With impure helium at low pressure no new lines came out, but an interesting result was obtained with the pure gas at a pressure of 30 cm. of mercury. This gave the yellow color characterizing helium, but when a trace of oxygen was admitted the yellow was replaced by a pale blue tinged with pink, which the spectroscope showed to contain the long-sought green line, 5577.35 Å. The possibility of this line having its origin in traces of carbon or mercury vapor was obviated by jacketing a length of the discharge tube with liquid air to condense any such vapors. Using the experience gained in the preliminary work, the investigators had a second discharge tube made. This was excited by a 60-cycle, 3-kv-a., 50,000-volt transformer. With pure helium or pure oxygen at different pressures no new lines were discovered nor any trace of 5577, except that this line appeared faintly in pure oxygen at low pressures when twice the usual current was sent through the primary of the transformer. The line 5577 came out best with a pressure of oxygen of

from 1 to 3 mm. and of helium from 20 to 40 mm., both gases being present in the tube. In mixtures of helium and nitrogen 5577 was not obtained, but the presence of helium caused the negative bands of nitrogen to become more prominent and these bands are known to appear in the aurora. In mixtures of helium, oxygen and nitrogen 5577, along with the nitrogen bands, appeared so that almost all of the auroral lines were obtained at once. In a mixture of neon and oxygen the line 5577 made its appearance. Thus neon acts like helium in enhancing this line.

The authors give as the best value of the wave-length of the green line 5577.35 Å.: "The agreement of the wave-length, together with the other physical characteristics of the line, particularly its sharpness and the wide fluctuations in its intensity, make its identity with the auroral green line almost a certainty." Since it appears in a mixture of helium and oxygen and also in a mixture of neon and oxygen, it is safe to attribute it to the common element in these two mixtures, that is, to oxygen. A conclusive argument in the same direction is its production in pure oxygen with very strong discharge currents. This line cannot be attached to any previously known band of oxygen, but must be attributed to some new spectrum of that element, developed by metastable helium.

"It can be shown that if diffusion in the atmosphere is considered to begin at or about 20 kilom. up, the composition at 110 kilom. should be approximately 20 of helium to 1 of oxygen. Thus, the relative composition of the atmosphere at the height of the maximum auroral excitation agrees very well with the values obtained from our observations."

The second paper emanates from the cryogenic laboratory at Leyden just as the first comes from the laboratory at Toronto, rich in means of producing low temperatures. Vegard on theoretical grounds was led to attribute the green line to solid nitrogen in the higher atmosphere. His present paper gives an account of the types of light emitted by several solidified gases at the temperature of liquid hydrogen. He finds that "solid nitrogen above 35.5° K. shows no luminescence." In the luminescence of solid nitrogen bombarded by cathode rays, he believes he has found the origin of the green auroral line, but his argument is not convincing. The light from the luminescent solid has a broad band of green light. This narrows into a diffuse line when the particles of solid nitrogen are taken smaller and in his opinion approaches the green line as a limit. It is, however, impossible to find in the numerous tables of wave-lengths of constituents of luminescent light recorded in this paper the desired 5577, to say nothing of 5577.35. After the conclusive evidence of the Toronto paper that the line is due to oxygen, the arguments adduced by Vegard to show that it comes from solid nitrogen seem futile. His paper none the less contains valuable observations.

G. F. S.

CURRENT TOPICS.

The Change of Mass of Silver Halogen Salts under Intense Illumination. P. P. KOCH and B. KREISS. (*Zeit. f. Physik*, Vol. 32, No. 5.)—Particles of silver salts were to be weighed, then subjected to illumination and again weighed. As the particles were very small, some kind of a micro-balance was called for. This was discovered in Millikan's method of studying the electrical charges on droplets by pitting the force of gravity acting downward against the upward acting force of an electric field established between two horizontal condenser plates. When a particle hovers in the condenser, neither rising nor falling, a simple relation connects its mass with four other quantities, two of which are constants, the acceleration due to gravity and the elementary quantity of electricity, while the remaining two, the strength of the electrical field in the condenser and the number of elementary charges on the particle, can be measured. Millikan has shown how to make the measurement of the last quantity by varying the charge on the particle through the use of X-rays. Quite aside from the results of this investigation this paper is of interest on account of its explanation of the way to use Millikan's condenser for the determination of small masses.

In the lower plate of the condenser was an aperture in which was inserted a Zeiss optical condenser, so that its upper surface was in the same plane with the upper surface of the lower plate of the electrical condenser. A film of soap was spread over the glass upper surface of the Zeiss combination to render it electrically conducting and thus to avoid distortion of the field between the two charged plates. The light from an arc lamp was concentrated within a circle of diameter .2 mm. in the space contained between the condenser plates. The illumination amounted to about 1500 times that in sunlight, being, on the average, 73×10^6 metre-candles in the absence of the soap. The authors calculate that the rise of temperature of the particles of silver salt is less than 10° C. in spite of the intense illumination. This surprisingly small elevation of temperature is obtained on the assumption that the particle loses heat only by conduction to the surrounding air, without convection playing any part, and is fundamentally due to the large area of the particle in relation to its mass. To examine further any possible effect of rise of temperature on the changes observed to follow illum-silver bromide was heated for three hours to 100° C. and then exposed to the light. It behaved just as it did before the heating. Thus it seems assured that whatever effects were produced by the intense illumination were due to the light itself and not to heat developed by it.

The film of soap mentioned above reduced the intensity of illumination at the particles to 67×10^6 metre-candles. Particles of silver iodide sometimes lost weight and sometimes gained, as was true

also of dust motes. Copper particles gained slightly while particles of barium sulphate gained a trifle, but all these changes mentioned up to this point range from .1 to 2.4 per cent. and lie within the limits of error. Quite otherwise is it with bromide and chloride of silver. In every case they lose weight, and the extent of the loss is so great that it is by no means in doubt. In fifty-eight minutes under the influence of illumination a certain specimen of silver bromide lost 27.6 per cent. of its weight, this being the largest percentage of loss observed. For silver chloride the largest loss is 14.3 per cent. In all cases where with silver bromide and chloride the connection between percentage of loss and duration of illumination was followed, it was found that at first the rate of loss is rapid, then it diminishes and becomes very slow as time passes.

The authors interpret the loss of mass of the particles as meaning that bromine or chlorine is given off. The masses of the particles used was of the order of 1 or 2×10^{-11} grams, and were therefore of about the mass of the particles of silver in photographic films.

G. F. S.

High-frequency Waves of Cosmic Origin. R. A. MILLIKAN. (*Science*, Nov. 20, 1925.)—At the meeting of the National Academy of Sciences, held at Madison, Wis., on November 9, 1925, Dr. R. A. Millikan, Nobel prizeman and director of the Norman Bridge Laboratory of Physics, Pasadena, presented this paper announcing conclusions of great importance. In 1903 Rutherford and McLennan found that the leak of an electric charge from an electroscope in an air-tight metal vessel was lessened by surrounding the vessel with a metal shield having thick walls. This was interpreted as meaning that some "penetrating radiation" of the atmosphere made its way into the unshielded vessel and ionized the contained air so that it became a conductor through which the charge of the electroscope escaped. At first this radiation was thought to originate in radioactive materials in the earth, but it was found that its intensity did not decrease with elevation above the earth as on this hypothesis it should have done. Indeed German investigators who sent up balloons discovered that the radiation decreased for the first two miles and then increased to eight times its value at sea-level when a height of 9 km. was attained.

In 1922 Millikan and Bowen sent up from Kelly Field remarkably compact recording electroscopes to a height of 15.6 km. The results made clear that the radiation at considerable elevations is really larger than at the surface of the earth, but the increase was only one-fourth as much as was to be expected from the German observations.

To study the penetration of the rays Millikan and Otis in 1923 went to the top of Pike's Peak with 300 pounds of lead and a cubical water tank 6 feet on a side. On the mountain the discharge of the electroscopes was twice as rapid as at Pasadena, yet from the effect

of screens on the radiation this seemed to be scarcely more penetrating than gamma-rays from radium. A snow storm lessened the rate of discharge of the electroscope by 10 per cent. This indicated that the rays concerned had their origin at no great distance from the place of observation. The expedition to Pike's Peak did not solve the problem of the penetrating rays but, on the contrary, it brought up the additional problem of the reason for the increase with elevation of the soft gamma-like rays responsible for the greater part of the discharge of the electroscope on the mountain.

In the summer of 1925 Professor Millikan with Mr. H. Cameron set out "to settle definitely the question of the existence or non-existence of a small, very penetrating radiation of cosmic origin. To bring to light the very penetrating radiation, if it existed, it was necessary to find at very high altitudes very deep snow-fed lakes, for any radio-active contamination of the water through its seepage through the earth would vitiate the results obtained by sinking electroscopes to different depths below the surface of the lake." Muir Lake, 11,800 feet above sea-level, close to Mount Whitney and hundreds of feet in depth, was selected, and there for ten days in August the two scientists worked. "Our experiments brought to light altogether unambiguously a cosmic radiation of such extraordinary penetrating power that the electroscope reading kept decreasing down to a depth of 45 feet below the surface. The atmosphere above the lake was equivalent in absorbing power to 23 feet of water, so that we had found rays, coming into the earth from outer space, so penetrating that they could pass through 45 plus 23, equalling 68 feet of water or the equivalent of 6 feet of lead, before being completely absorbed. . . . The most penetrating X-rays which we produce in our hospitals can not go through half an inch of lead. Here were rays originating somewhere out in space, at least a hundred times more penetrating than these." All the Muir Lake results were confirmed by experiments made at Arrowhead Lake, 300 miles away and 7000 feet lower.

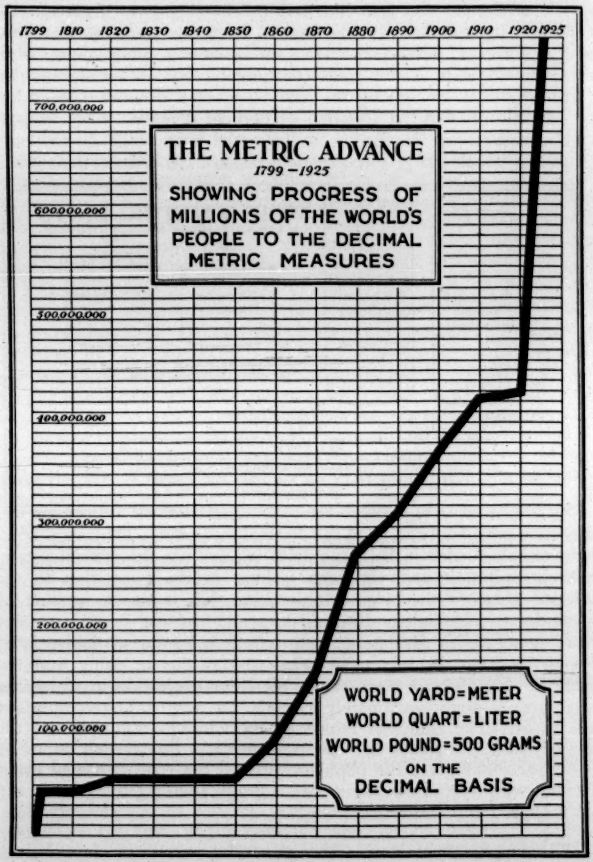
These cosmic rays seem to traverse space in all directions, since no change in them was noted throughout the twenty-four hours of the day. They are not all of the same wave-length but embrace about an octave. From a formula not certainly applicable but yet regarded as well worthy of consideration is deduced the wave-length of the shortest waves. This is .0004 Ångström, 1/50 of the length of the shortest gamma-rays hitherto known and 1/10,000,000 of the wave-length of ordinary light. Since the most penetrating radiation previously known, the gamma radiation from radium and thorium, appears as the product of nuclear transformation inside of the atom, it is reasonable to attribute the new penetrating radiation to a similar origin, though the energy transfers involved must greatly exceed those that take place in the production of gamma-rays. "We can scarcely

avoid the conclusion, then, that nuclear changes having an energy value perhaps fifty times as great as the energy changes involved in observed radio-active processes are taking place all through space, and that signals of these changes are being sent to us in these high-frequency rays." The author inclines to the belief that in the capture of electrons by positively charged nuclei is to be sought the process responsible for the penetrating rays. If it be that all space is not traversed in all directions by these rays, the alternative hypothesis must be adopted that electrons traverse space in all directions with high speed and in the upper layers of the atmosphere generate the rays to be accounted for. This explanation "too, fills space with rays of one sort or another, travelling in all directions with the speed of light. From some such conception as this there now seems to be no escape." When the penetrating rays impinge on the earth, by the Compton effect they produce soft scattered radiation of the kind that was in evidence on Pike's Peak. On this mountain there was more of the soft radiation than in Pasadena because at the higher altitude there was more of the penetrating radiation to be transformed, it not yet having been subjected to the absorption of the air below the level of the mountain top. The limits of the spectrum of radiation have by this investigation been enormously extended, though the earlier observers are deserving of great credit. G. F. S.

Flames of Atomic Hydrogen. I. LANGMUIR. (*Science*, November 20, 1925.)—As early as 1911 Langmuir concluded that hydrogen is to a great extent turned into atomic hydrogen at temperatures of 2500° K. or higher. Further examination convinced him that by heating a platinum or tungsten filament above 1300° K. in hydrogen at low pressure, atomic hydrogen is formed. It was calculated that the heat of combination of two grams of atomic hydrogen is 90,000 small calories. Later he obtained the gas dissociated into the atomic form by sending 20 amperes of current from one tungsten rod 6 mm. in diameter to another in a stream of hydrogen. The resulting arc of a red color was not more than 2 cm. in length with voltages from 300 to 800. "Iron rods 2 or 3 mm. in diameter melted within a couple of seconds when they were held 3–5 cm. above the arc. By directing a jet of hydrogen from a small tube into the arc, the atomic hydrogen could be blown out of the arc and formed an intensely hot flame of atomic hydrogen burning to the molecular form and liberating 90,000 calories per gram molecule—about 50 per cent. more than in an oxy-hydrogen flame." Molybdenum and tungsten were melted when held close to the arc. Quartz was harder to melt than the first of these.

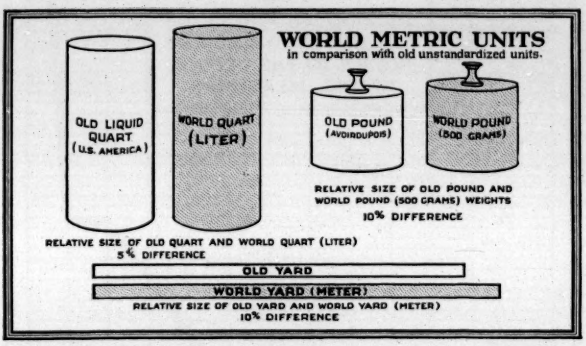
By the process just described iron can be welded or melted with the avoidance of carbon, nitrogen and oxygen, and also alloys of chromium, aluminum, silicon or manganese. G. F. S.

Progress of the Metric System.—An important international event is the signing of a commercial treaty between Japan and Russia, whereby both countries have agreed to adopt the metric system.



By this, the whole of Continental Europe is now under that system. Almost the whole of the Western Hemisphere is also using it, so that the United States and the British Empire are the only important

powers standing out. A recent pamphlet issued by the organization known as the "Central Manufacturing District of Chicago" contains data showing the immense number of people who are now using metric measures, and also illustrations showing how slight are the volume, length and weight differences from our common standards, which, however, have complicated and annoying subdivisions, while the decimal system is simple and convenient. It is rather curious that a nation which was among the first to adopt a decimal coinage has persistently resisted the adoption of decimal divisions in its weights and measures. It is further to be noted that while British and American peoples have so obstinately resisted the change, their scien-


WORLD METRIC UNITS
in comparison with old unstandardized units.
OLD LIQUID QUART (U.S. AMERICA)
WORLD QUART (LITER)
OLD POUND (AVOIRDUPOIS)
WORLD POUND (500 GRAMS)
RELATIVE SIZE OF OLD POUND AND WORLD POUND (500 GRAMS) WEIGHTS
10% DIFFERENCE
RELATIVE SIZE OF OLD QUART AND WORLD QUART (LITER)
5% DIFFERENCE
OLD YARD
WORLD YARD (METER)
RELATIVE SIZE OF OLD YARD AND WORLD YARD (METER)
10% DIFFERENCE

tists have universally adopted the decimal measures. The chemistries, for example, issued in both countries, always use the metric system. Misrepresentation had not been lacking in the opposition to the reform. One of the original objections, that it was a product of revolutionary, irreligious France, does not find use now, but some years ago, *English Mechanics*, in an attack upon the system, printed a map to show the respective areas of the nations using and not using it. By giving a map on the Mercator projection in which the polar area is disproportionately extended, a most unjust comparison was made. The pamphlet issued by the Chicago organization (the text of which is furnished by the All-American Standards Council of San Francisco) gives the population of all the countries now using decimal weights and measures, also a graph showing the gain in use since 1799, when France adopted it. H. L.

The Oppau Explosion.—Though several years have elapsed since the explosion at the nitrogen-fixation plant of the BASF at Oppau (September 21, 1921) the cause remains unexplained, or, at least, not made public by the experts of the plant. The explosion occurred

in a mass of about 4500 tons of an intimate association of ammonium sulphate and nitrate corresponding closely to the formula of one molecule of the former to two of the latter. While some of the stored mass which was termed at the works a "silo," presumably because intended for fertilizer purposes, may have been decomposed by the explosion, it is stated that a very large amount of unchanged materials was gathered from around the crater. A great deal of property damage and much loss of life occurred. German authorities ascribed the accident to the mass of sulphate-nitrate salt. This had become compacted and it was the habit of the plant to blast out with special explosives the material needed from time to time, but no such blasting was going on at the time of the accident. There are not wanting persons who believe that the explosion was premeditated with a view to destroying some portions of the plant that held important secrets, and that the occurrence was premature, but no proof of this is forthcoming.

The possibility of explosion of the Oppau salt, as it may be called for convenience, was subjected to careful, exhaustive and critical investigation by British authorities, the results of which were published in the *Transactions of the Faraday Society* (1924, **20**), and issued also as a separate pamphlet which by courtesy of the Society has been sent to this JOURNAL, and from which the following data are taken: About a ton of the salt of the same composition as that which was in store at the time of the explosion was forwarded to England and used in a great variety of tests. Every effort was made to cause the salt to explode violently by the use of initiators, compression, heat and other means known to experts in explosives. All experiments failed to show that the salt had any real marked explosive property other than that due to ammonium nitrate, which, as might be expected from its composition, is a high explosive when certain initiators are used. It was stated by German authorities that some time preceding the explosion the practice of mixing the two salts in solution and then evaporating was substituted by a method of squirting the nitrate onto a conveyor band and adding the sulphate by hand. This, it is believed, might produce incomplete mixture and cause some of the nitrate to be collected in a separate, somewhat bulky, mass.

The investigation was carried out very thoroughly, physical and chemical data of all types being ascertained. These are fully set forth in the paper, but the point interesting to chemists at large is the question as to whether a large mass of ammonium sulphate-nitrate consisting, as was ascertained, of practically a definite compound of the two, could suddenly assume the nature of a high explosive. The investigation as noted above negatives this view. It has been claimed by German authorities that one of their experts, Poppenburg, has succeeded in exploding Oppau salt, but careful repetition of his experiments as reported failed to confirm the statement.

The problem of this explosion has interest beyond the mere search for an explanation. In a suggestive way it may be pointed out that if it had occurred between 1914 and 1918, it would have probably seriously crippled the German forces, as the plant was an important source of nitrates. In a scientific sense, it may be possible that while the moderate amounts of the salt, a few hundred pounds, that were used in the British experiments did not respond to any initiators, the result might be different with many tons of material such as were in store in the silo. Explosives are eccentric. In this connection the properties of picric acid may be noted. Ordinarily this is regarded as involving no danger. For many years it was carried in quantity from place to place, used in chemical laboratories and in dye-houses without any thought of danger, yet under the urge of a proper initiator it becomes a very high explosive. Ammonium nitrate, indeed, is in the same category. No serious restriction is made on its sale, and for many years it has been used in the manufacture of nitrous oxide, under conditions which seem to be liable to arouse any latent activity. The whole subject of explosion and of the properties of explosives is an attractive and important department of physics and chemistry. The British authorities are deserving of much credit for their painstaking and thorough study of the Oppau salt problem, and the Faraday Society has contributed to the progress of an important department of chemistry by broadcasting through its *Transactions* the results obtained. H. L.

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